BITUMINOUS SUBSTANCES

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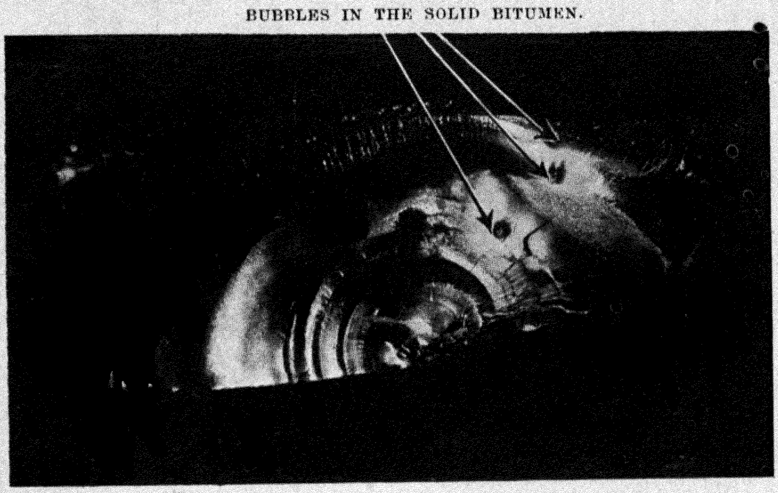

Conchoidal Fracture of Bitumen (E-Grade Mexican), showing Concentric and Radial Cracks, and Bubbles.

Photographed on a process plate (H. and D., 8), *f* 32; twenty minutes exposure, with oblique illumination from a half-watt lamp.

BITUMINOUS SUBSTANCES

SCIENTIFIC PROGRESS OF PRACTICAL IMPORTANCE DURING THE LAST FIFTEEN YEARS

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WITH A FOREWORD BY

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TO THE MEMORY OF

OTTO HEHNER

CHEMIST AND FRIEND

IN GRATEFUL AFFECTION

FOREWORD

Of all the various products derived from crude petroleum, asphalt or bitumen is that which was earliest known and utilised by man. Not only are records of its use found in the works of the earliest historians, but actual examples of its use are to be found in our museums.

Its uses are to-day much more varied, and its importance to the life of the community much greater, and its applications and value are ever increasing.

Future historians will undoubtedly record that the first quarter of the present century marked an epoch characterised by great and new developments in many directions. Among the most important of these is the fundamental change in transport methods brought about by the development of the high-speed internal combustion engine, which development has been rendered possible by ample supplies of suitable motor fuel consequent on the rapid expansion of the petroleum industry.

This change has resulted in the great development of road transport, in consequence of which roads are now called upon to bear much heavier and more quickly moving loads than formerly, which loads have proved more than they can bear. It seems curious that the damage to roads indirectly brought about by a petroleum product can be repaired or made good by another product from the same source. Asphalt or bitumen has proved itself an invaluable material for the construction of roads which will stand up to the heaviest traffic they are likely to be called upon to bear.

Apart from its value as a road-making material, bitumen is largely used for such diverse manufactures as those of roofing felt, waterproof papers and fabrics, paints and protective coatings of many varieties, electric-insulating material, fusible cements, and so forth.

Although the earliest known and used product of crude petroleum, it is from the chemical standpoint the least understood to-day. This is, of course, owing to the relatively complex nature of the chemical substances which constitute this useful material. It may be safely said that definite chemical knowledge of the constituents of crude petroleum is confined to the hydrocarbons with low molecular weight and boiling-point; those which constitute motor spirit in fact. The higher the boiling-point of these hydrocarbons, the more complex their chemistry becomes.

The author, while fully aware of the difficulties attending this subject, has made an effort to bring together and to discuss what is known of the chemistry of bitumens, and has endeavoured to correlate as far as possible their chemical composition with their physical behaviour and properties. From the industrial point of view the establishing of definite relations between the chemical and physical properties of bitumens as examined in the laboratory with the actual behaviour of the material in its industrial applications is a point of very great importance.

While much still remains to be done in this direction, the author has succeeded in putting forward and correlating much information, some hitherto unpublished, which will not only help to throw light on this interesting question, but also be of practical service to all users of this interesting product.

J. KEWLEY.

January, 1925.

PREFACE

This book is for those who wish for information about the present position of scientific knowledge concerning bituminous substances, and for those who desire to see round the subject as well as into it.

For this reason, space has not been restricted when dealing with history and nomenclature—even though the latter is as dull as the former is interesting. Care, too, has been given to the collation of useful information that has appeared in scientific and technical literature during the period of years that roughly covers that of the rise of the asphalt pavement into an important factor in the development of transport.

Further, there has been included information relative to the properties and the testing of bitumen, in order to save the expenditure of time and trouble in ascertaining those fundamental facts that should be readily at the service of investigators. Some of these matters are referred to in the usual textbooks on the subject, but few experimental figures are available to indicate the extent to which results are modified by the influence of conditions and treatment.

Most of these last facts have been ascertained in the laboratory of Messrs. Highways Construction, Ltd., and to this firm the author tenders his thanks for the kind permission to publish them. Full acknowledgments, too, are given to the chief chemist, Mr. D. M. Wilson, M.C., B.Sc., A.I.C., and to Mr. E. W. Bolton, B.Sc., A.I.C., both of whose excellent practical work and ideas were valuable weapons in attacking the details of the various problems.

Great appreciation is also felt by the author for the most courteous permission accorded by the Council of the Institution of Petroleum Technologists to reproduce the recently, tentatively established standard methods of testing this class of substance.

P. E. S.

January, 1925.

BITUMINOUS SUBSTANCES

CHAPTER I

HISTORICAL INTRODUCTION

THE human history of bitumen begins about 12,000 years ago, with the late Stone Age man who lived in the area of what is now the Mediterranean. By the time that he had become indigenous to that locality, he had developed from his most primitive beginnings to the point of becoming a semi-permanent resident in whatever land he found himself. He still had not yet learned the use of any metals, but employed implements of flint (in the making of which he had acquired considerable skill) and of bone. He made rough pottery, he sowed grain and raised cattle and pigs, and he had already acquired the companionship of the dog; his reaping hook was of flint when he could get it, otherwise it consisted of an earthenware scythe.

He carried with him the memory of one of those tremendous natural disasters that for ever stamps itself on the mind of man, which may have been one of the last of the series of cataclysms that drove the land of Atlantis below the Atlantic Ocean, and sent wave after wave of its inhabitants far afield in search of another home in safety. So great was this impression that this memory became associated with a subsequent and local inundation which was thereby magnified to the importance, to us, of the Noachian Flood (usually considered to be about 2500 B.C.). Although the Vulgate uses the word "bitumen" for the material used to render Noah's Ark watertight, it is possible that this may refer to pine pitch, which was known at the time. On the other hand, the Babylonian story that is given in the Gilgamesh epic,[1] one of several that are closely comparable to that of Noah, does employ a term which is translated "bitumen." This Babylonian Noah, Pir-napishtim, "smeared it with bitumen inside and pitch outside. . . ."[194]

From this region Mediterranean man spread slowly eastwards, and reached Mesopotamia, where a gap of some few thousand years occurs in datable records till a mysterious non-Semitic race, the Sumerians, first appear in the South. Their origin is uncertain, and although excavations have revealed an early Neolithic agricultural stage directly beneath the earliest Sumerian foundations, the Sumerians appear to be a different race from that over which they spread. They possibly came from the Mesopotamian-Persian frontier from the Elamite plateau in the region of Susa. The Sumerians scratched their earliest records, about 6000 to 7000 B.C., in characters on clay, which have been deciphered. The language is possibly connected with the Basque language in France along the Pyrenees, which is of peculiar significance as the Basques are recognised as being the purest remnant of Neolithic man that exists at the present time. The Sumerians slowly and definitely developed their culture to a remarkable degree. They became very skilful hydraulic engineers, and irrigated their fields. Their religion demanded the raising up of tower-like temple buildings, one of which, at Nippur, is supposed by tradition to be referred to in the story of the Tower of Babel. They fought amongst themselves, but for long remained unconquered by external enemies, and developed their civilisation, their writing, and their shipping through a period that may be as long as the whole period from the days of Moses (about 1300 B.C.) to the present time. They developed also considerable artistic ability, and in some of their statues the eye-sockets were made hollow, and there is good reason for thinking that they were filled with bitumen in order to secure in place the bits of mother-of-pearl, ivory, or white limestone which represented the eyes themselves. Their vases, too, were sometimes ornamented with the aid of bitumen[2] as the cementitious material. Most remarkable is the famous sculptured votive offering consisting of an artificial mixture of bitumen and clay, stamped with the heraldic device of Lagash (2850 B.C.).[3]

About the same time, the early Persians also were employing bitumen as cementitious material in the eye-sockets of figures of little alabaster animals. They also carved vases and representations of animals from the solid material, and decorated them with elaborate ornamentation.[4] An analysis of the material shows it to be a bituminous limestone, containing 25 per cent. of bitumen, of the same composition as has recently been found at Hit, on the Euphrates.

Along the western fringe of this Empire certain Semitic nomadic tribes became united together under a great leader who attacked and beat the Sumerians and fused with them. This man, Sargon I., founded the Sumerian-Akkadian Empire which lasted for 200 years; and, as has happened many times in history, the barbaric, warlike, nomad tribe beat the more peaceful and refined city dweller in battle, but became absorbed by him owing to his superior degree of culture.

A remarkable record ascribed to this King (2750 or 3750 B.C.) has been deciphered, showing acquaintance with the use and properties of bitumen, which has a particular significance which will be referred to later.

"Sargon, the mighty king, the king of Agade am I, my mother was lowly, my father I knew not, and the brother of my father dwells in the mountain. . . . My lowly mother conceived me, in secret she brought me forth. She set me in a basket of rushes, with bitumen she closed my door; she cast me into the river which rose not over me. The river bore me up, unto Akki, the irrigator, it carried me. Akki, the irrigator, with . . . lifted me out, Akki, the irrigator, as his own son . . . reared me. Akki, the irrigator, as his gardener appointed me. While I was a gardener, the Goddess Ishtar loved me. And for . . . four years I ruled the kingdom."[5]

Historians call him a usurper.

This empire was finally overwhelmed by the great King Hammurapi (2100 B.C.), whose capital was a small town on the Euphrates, named Babylon; and this was the start of the first Babylonian Empire. In another hundred years, fresh nomad tribes possessing the enormous advantage of the horse chariot swarmed down against Babylon and took it, but did not hold it very securely. These people were the Assyrians, whose headquarters were up in the north and whose more important cities were those of Assur and Nineveh. There had been constant fighting in the past with Sargon I., and strife continued between themselves and the semi-conquered Babylonians. And Assyrian power further extended towards Syria and expanded south-west towards the land of Canaan.

Later, after the Assyrians had established themselves more firmly in Babylon and had founded the new Assyrian Empire, a usurper seized the throne and sought to ingratiate himself with the Babylonians by taking the title of Sargon II. He was remarkable in that he seems to have armed the Assyrian forces for the first time with iron weapons, and it was he who undertook the deportation of the Israelites from their land.

It was only after the 400-year delay in completely conquering Babylonia, Syria, and Palestine (as we now call it), that the Assyrians were able to free their strength and achieve the capture of Egypt. The failure of the first attempt to do this by the army of Sennacherib, the son of Sargon II., was due to its being so dramatically smitten by a pestilence, quite possibly malaria, on the very borders of Egypt, an event which was described in that curious and vivid Biblical sentence, "and when men arose early in the morning, behold, they were all dead corpses."

The wheel of fortune continued to revolve in these parts. Fresh nomadic tribes, this time from the south-east, the Chaldeans, united with the Medes and Persians from the north and captured Nineveh in 606 B.C. This Chaldean Empire, with its capital at Babylon, was ruled over by the famous Nebuchadnezzar the Great, and his successors, till 539 B.C., when it fell before the attack of Cyrus, the founder of Persian power.

In the days even before Sargon and onwards, bitumen appears to have been in regular use in architecture and civil engineering. It must be realised that in certain directions the arts and science were continuously and highly developed. A fine stone bridge crossed the Euphrates; processional ways and boulevards were laid out. It became a common thing in Nineveh, Nimroud and Babylon for city and palace walls and private houses to be built of stones and bricks set in bitumen; and in Nineveh has been discovered a regular damp-course underneath a stone floor.[12] A water conduit and a drain were found[6] to have been constructed with the aid of bitumen. Several inscriptions have been discovered relating to the use of bitumen in connection with buildings in Babylon by Nebuchadnezzar, but the most remarkable of all, as an anticipation, was the use of this construction for roadway purposes—for a processional street leading from the King's palace in honour of Marduk, the most powerful local god of Babylon, and of Nabû, who was second only to Marduk and not always that.

The inscription relating to this road reads:

"Nebuchadnezzar, King of Babylon, he who made Esaglia and Esida glorious, son of Nabopolassar, King of Babylon. The streets of Babylon, the Procession Streets of Nabû and Marduk my Lords, which Nabopolassar, King of Babylon, the father who begat me, has made a road glistening with asphalt and burnt bricks; I, the wise suppliant who fear their lordship, placed above the bitumen and burnt bricks a mighty superstructure of shining dust, made them strong within with bitumen and burnt bricks as a high-lying road. Nabû and Marduk, when you traverse these streets in joy, may benefits for me rest upon your lips; life for distant days, and well-being for the body. Before you I will advance (?) upon them (?). May I attain eternal age."[7]

Not only in the construction of dwellings, palaces, temples, and hanging gardens was bitumen employed, but in big engineering works, as the following record, also by Nebuchadnezzar, shows:

"In Babil, my favourite city that I love, was the palace, the house, the marvel of mankind, the centre of the land, the shining residence, the dwelling of Majesty, upon the Babil place in Babil, from Imgur-bel to the eastern canal Libil-higalla, from the bank of the Euphrates to Aiburšabû, which Nabopolassar, King of Babylon, my father, my begetter, built of crude bricks and dwelt in it—in consequence of high waters its foundations had become weak, and owing to the filling up of the street of Babil the gateway of that palace had become too low. I tore down its walls of dried brick, and laid its corner-stone bare, and reached the depth of the waters. Facing the water I laid its foundation firmly, and raised it mountain high with bitumen and burnt brick. Mighty cedars I caused to be laid down at length for its roofing."[8] "That no assault of battle may approach . . . for 490 ells of land I made for a protection two mighty walls of asphalt and burnt bricks . . . and made upon it a lofty seat for my royal dwelling of asphalt and burnt brick. . . ."[9]

Thus Nebuchadnezzar, profiting by the experience of his father, built a retaining wall, not of dried clay bricks, which, owing to their lack of waterproof properties, had failed to hold back the waters of the Euphrates, but of burnt bricks and asphalt, as originally practised by Sargon, apparently with satisfactory results.

The prevailing method of constructing walls[10] in Babylonian times consisted in laying in rotation a course of bricks, then a layer of asphalt, and then a layer of clay; and between the joints in each course was a mixture of clay and asphalt. In every fifth course, however, the clay was replaced by a matting of reeds of which the sole remains to-day is its impression in the asphalt.

In addition to actual constructional work, wooden walls and towers were painted with bitumen for protection against the weather, in spite of the danger of fire, as Xenophon later pointed out. This writer also remarked on a wall in Media being built of bricks and bitumen, which shows for how long the method of Babylon was found to be valuable.

In Egypt there is not so much to record, but what there is, is most striking. This region also was founded on the early Neolithic culture, and whilst its subsequent history was roughly similar to that of Mesopotamia, it may not have been quite so warlike nor so complicated.

Bitumen was employed in Egypt[11] (about 2500 B.C.), for the preservation of mummies, and is extensively found in their wrapping. The association is so close that the word "mummy" is derived from the Arabic word for bitumen; and the Arabic word for "mummy" is more strictly, "bituminised thing." It has also been found to have been used for rendering watertight cisterns and grain stores. When this practice is traced back to its earliest evidence, we find ourselves again in the presence of Stone Age man. A grave was found in which were all the evidences of Neolithic culture—implements, orientation, posture. When the grave was opened a strong smell of bitumen was observed (after many thousands of years), and the body, skin, and hair were so well preserved as to force the conclusion that the bitumen was the material used for assisting in the prevention of normal dissolution.

Another point which need hold us is in connection with the exodus of the children of Israel from Egypt. One of the most significant figures in the ancient history of the Near East is that of Moses, and it is bewildering to learn that of Moses there is no unmistakable contemporaneous Egyptian record. There is no doubt that around his name has grown a large body of myth and legend, just as myth of wisdom has gravitated to Solomon, and myth of music and song-writing has collected round David. Of the charming story of Moses being found by Pharaoh's daughter in his little ark of bulrushes caulked with bitumen, there is also no word; but we remember the record, more ancient by over 1,000 years, in connection with Sargon I. As, however, Moses was sufficiently real to be considered the leader of the Exodus in the neighbourhood of 1300 B.C., we can follow into the land of Canaan, which is the third area of our present interest.

The history of this region is one of almost continuous and disastrous strife, with only the one single short space of time of comfort and luxury that occurred in the earlier days of Solomon. The rest was spent in fighting the surrounding tribes; in the most suicidal of civil wars; and in being fought over by the great powers of the north and south striving to reach and conquer one another. In this last phase, this territory was the cockpit of its region, just as Belgium has always been the cockpit of Europe, and for closely similar politico-geographical reasons. All this is of importance at the present moment, in that when Nebuchadnezzar carried the Israelites to their Babylonian exile, there occurred the main crushing disaster, which, however, certainly led to the birth of the most dramatic religious revolution of the world.

In Babylonia the Israelites met a race passionately devoted to their own history. The example fired them to put their own on record, with the result that the compilation of the so-called Five Books of Moses was begun, leading to the subsequent development of the Bible (as we know it), and all that it means and has meant. For the first time an orderly record was made of events which happened 700 years before; and it is this long gap of verbal tradition that has made it so difficult to extract trustworthy and recognisable historical facts from the Bible. Undoubtedly, the period and the locality where the account was undertaken are the cause of the introduction into the newly compiled records of much Babylonian myth, such as the account of the Garden of Eden, the story surrounding the building of the Tower of Babel, the pretty account of (the Babylonian) Noah, and the Sargon story which was grafted on to the memory of Moses. It is the result of this 700 years' lapse between occurrence and record which, together with doubtful meanings and imperfections of translation, makes us wonder, at first, what is meant when the Bible refers to the stones (which may be bricks) of the Tower of Babel being cemented together with "slime." Doubt becomes lessened when mention is made of "slime-pits" in the valley of Siddim; and final elucidation is obtained from the Septuagint, which uses the Greek-like word "asphaltos," and from the Vulgate, which employs the very word "bitumen."

The valley of Siddim is almost certainly the valley of the Dead Sea, and many are the records of bitumen rising to its surface from the depths, from ancient times onwards. It was gathered by the natives and despatched to Egypt for the embalming of bodies, because, as writes Diodorus Siculus of Sicily (B.C. 80): "Without the mixture of this material with other aromatics it would be difficult for them to preserve these for a long time from the corruption to which they are liable." A later interesting testimony is that of Sir John Mandeville (about A.D. 1356) from a description of his "Voiage and Travayle," published in 1568. He writes: "Two myle from Jerico is flom Jordan; and ye shall wete that the Dead Sea departheth the lands of Jude and Araby, and the water of that Sea is right bitter, and this water casteth out a thinge that men call Aspatum, as great pieces as an horse. . . ."

Passing still further down the highroad of history, we reach Herodotus, who wrote, about the year 450 B.C., of his having seen pitch drawn from springs in the waters of the island of Zante by means of a descending pole to which a myrtle branch was fixed, which, when drawn up, bore the material sticking to the branch. He mentions also lumps of asphalt being carried down by the waters of the Is, which discharges into the Euphrates by the city of Is, probably the city of Hit, where bitumen is still found in considerable quantities. He also refers to a well near Susa which produces asphalt, salt and oil. At Elam asphalt is still collected out of a well in the manner described by him.

In Roman times asphalt was used to protect images from the action of the weather, and also was employed medicinally for curing boils, inflammation of the eye, coughs, asthma, blindness, epilepsy and other ills. Importance was evidently attached to its purity, as it was considered that pitch had been mixed with it if its appearance was not glossy and black. It was sold under the name of "mummy," and was actually scraped from them. Although the ancient Jews employed bitumen for its medicinal properties, it was from the first century A.D. onwards that it spread into general use, particularly about A.D. 370 in Arabia.

From these times forward records diminish in interest except for the discovery of the asphalt lake in Trinidad by Sir Walter Raleigh in 1595; hereafter the history of bitumen is modern history.

Note.—At the last moment there has come to the notice of the author a paper by A. Lucas, O.B.E., F.I.C., formerly Director of the Chemical Department of Egypt (*Journ. Egypt. Arch.*, 1924, **10,** 132). In it Mr. Lucas states that he has frequently searched for bitumen or mineral pitch in the black material of embalmed mummies, and has never found it to have been used at any period. As a general rule, one kind or another of resin was employed for the purpose.

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APPENDIX B

STANDARD METHODS OF TESTING PETROLEUM PRODUCTS: CLASS VIII.—ASPHALTS

(Institution of Petroleum Technologists: 1924. Slightly modified in wording for the sake of continuity.)

SPECIFIC GRAVITY.

I.P.T. Serial Designation—A. 1.

Solid Materials.—Where applicable the method of displacement of water by a known weight of material shall be employed.

Other Materials.—For semi-solid materials the specific gravity shall be determined in a graduated flask of not less than 100 c.c. capacity, or a special pyknometer, the material being heated to promote fluidity. The contents of the flask may be cooled to 60° F. if their nature permits, and the volume to the graduation mark adjusted with a little more of the melted material. Where this cooling is not practicable the specific gravity shall be determined at higher temperatures, the material being kept fluid, and the proper temperature correction made. (See pp. x. and 1 in the I.P.T. volume.)

SULPHUR.

I.P.T. Serial Designation—A. 4.

The determination shall be made in a suitable bomb calorimeter with such modifications of the preparation of the sample for combustion in the bomb as its nature requires.

The inner surfaces of the bomb shall be of materials that are chemically and physically resistant to the process and products of combustion.

The gaskets, insulating materials, etc., shall not be liable to action with the products of combustion in such a way that any increase or decrease of the sulphur content of the liquid in the bomb shall arise.

Particular attention is directed to lead gaskets, which have been found to form lead sulphate if any appreciable area is exposed.

The ignition wire shall be of fine platinum (0·15 mm. diameter is suitable).

Distilled water and all reagents should be sulphur free. If this is found not to be the case, a blank shall be made and the results properly corrected.

METHOD.

The weight of the sample to be used shall be not less than 1 gram. Ten c.c. of distilled water shall be placed in the bomb. The oxygen pressure shall be not less than 25 atmospheres. The bomb shall be immersed in cold water before firing.

After firing, the bomb shall remain in the water for 10 minutes. This allows practically complete absorption of the oxides of sulphur by the water.

The gases shall be allowed to blow off slowly into the air. The bomb shall be emptied into a beaker and the interior, including cover and all internal parts, washed out thoroughly with distilled water.

If the collected contents and washings are not clear they shall be filtered and the filter paper thoroughly washed with distilled water, the washings being added to the filtrate.

The washings, filtrate, etc., should not exceed 300 c.c.

Precipitation of the Sulphur.—Two c.c. of concentrated hydrochloric acid and 0·5 gram of pure sodium peroxide (Na_2O_2) shall be added, and the solution well boiled.

Ten c.c. of barium chloride solution (100 grams $BaCl_2 2H_2O$ per litre) shall be boiled in a test tube and slowly added to the boiling liquors. Boiling shall be continued for at least 15 minutes.

The solution shall be kept on a hot plate or steam-bath for not less than 4 hours. It is recommended that it shall stand all night with suitable cover to prevent undue loss by evaporation.

The paper and precipitate shall be washed with water until free from all traces of chlorides, and finally with a solution of ammonium nitrate (10 per cent.), and dried. This treatment assists combustion of the paper and prevents reduction of the barium sulphate. The paper shall be burnt off and the precipitate and paper ash ignited and weighed in the usual manner.

FLASH-POINT AND FIRE-POINT (OPEN).

I.P.T. Serial Designation—A. 7a.

The apparatus shall be the Pensky-Marten cup (without cover).

METHOD.

The thermometer shall be fixed so that the centre of its bulb is in the vertical axis of the cup and ½ inch below the filling line.

The test flame shall be of the same size as that of the standard head—0·16 inch (0·4 cm.)—and shall be fixed at the vertical axis of the cup and at a level with the upper edge of the cup.

No stirring shall be employed, and the greatest precautions must be taken to screen the apparatus from draughts. It is recommended that the test shall be carried out in a fume cupboard free from air currents.

The rate of heating shall be 10° F. per minute.

The *flash-point* shall be taken as the temperature when a flash appears at any point on the surface of the oil. No correction shall be applied for the exposed mercury thread.

FIRE-POINT.

To determine the fire-point the heating shall be continued under the above conditions until the oil ignites and continues to burn for 5 seconds. This temperature shall be termed the fire-point.

MOBILITY.

I.P.T. Serial Designation—A. 8.

This shall be determined at suitable temperatures in the Redwood No. II. viscometer (arranged to permit of temperatures up to 420° F. being obtained). The following temperatures are recommended: 200°, 300°, 400° F., and for flux oils 200° F.

CARBON RESIDUE.

I.P.T. Serial Designation—A. 9.
A.S.T.M. Serial Designation—D 47—21 *T.*

Apparatus (Fig. 38).

A. A porcelain or silica crucible, wide form, glazed throughout, 25 to 26 c.c. capacity, 46 mm. diameter.

B. An iron crucible, 45 c.c. (1½ ounces) capacity, 65 mm. in diameter, 37 to 39 mm. high with cover, the cover being provided with one opening of 5 to 6 mm. diameter.

C. A wrought-iron crucible with cover, about 180 c.c. capacity, 80 mm. diameter, 58 to 60 mm. high. At the bottom of this crucible a layer of sand is placed about 10 mm. deep, or enough to bring the inner iron crucible with its cover on nearly to the top of the wrought-iron crucible.

D. Triangle, pipe stem or silica tube covered, projection on side to allow flame to reach the crucible on all sides.

E. Sheet-iron or asbestos hood provided with a chimney about 2 to 2½ inches high, 2⅛ inches in diameter, to distribute the heat uniformly during the process.

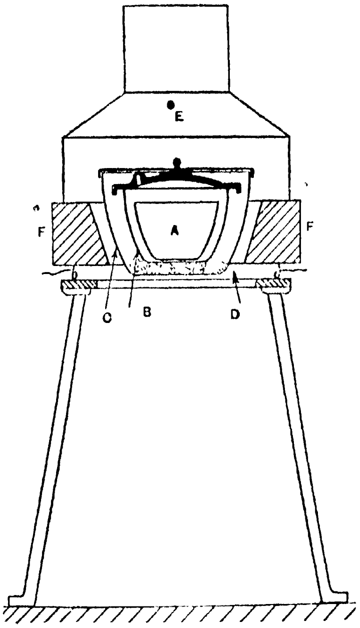


Fig. 38.—Carbon Residue Apparatus.

F. Asbestos or hollow sheet-iron block, 6 to 7 inches square, 1¼ to 1½ inches high, provided with opening in centre 3¼ inches in diameter at the bottom and 3½ inches in diameter at the top.

METHOD.

The tests shall be conducted as follows: 10 grams of the sample to be tested shall be weighed in the porcelain crucible A, which is placed in the iron crucible B. These two crucibles are set in the larger iron crucible C, being careful to have the crucible B set in the centre of the iron crucible, covers being applied to each of the iron crucibles. Place on triangle and suitable stand with asbestos block, and cover with sheet-iron or asbestos hood in order to distribute the heat uniformly during the process.

Heat from a Bunsen or other burner shall be applied with a high flame surrounding the large crucible C until vapours from the sample begin to ignite over the crucible, when the heat shall be moderated so that the vapours come off at a uniform rate. The flame from the ignited vapours should not extend over 2 inches above the sheet-iron hood. After the vapour ceases to come off, the heat shall be increased as at the start and kept constant for 5 minutes, making the lower part of large crucible red hot, after which the apparatus shall be allowed to cool somewhat before the crucible is uncovered. The porcelain crucible is removed, cooled in a desiccator, and weighed.

The entire process should require one-half hour to complete when heat is properly regulated. The time will depend somewhat upon the kind of material tested.

ASH.

I.P.T. Serial Designation—A. 10.

A suitable quantity of the sample shall be slowly carbonised in an open platinum dish and the residue incinerated until all carbon has been burnt off.

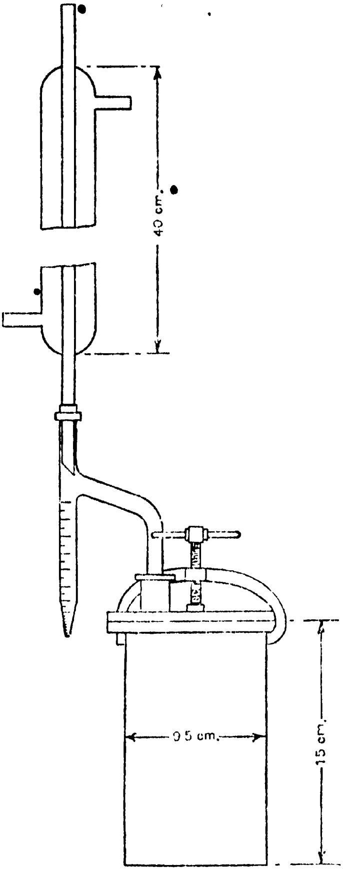


FIG. 39.—WATER IN ASPHALTIC SUBSTANCES.

WATER.

I.P.T. Serial Designation—A, 14.
A.S.T.M. Serial Designation—D 95—21T.

The apparatus generally desirable consists of a metal still, preferably of copper (Fig. 39), having a faced flange at the top of which the head is tightly attached by means of a clamp. The head is also of metal, brass, or copper, and is provided with a tubulation of 1 inch diameter.

A heavy paper gasket moistened with the diluent shall be inserted between the lid and flange before attaching the clamp.

The burner used with the metal still shall be a ring gas burner of 4 inches (100 mm.) inside diameter.

The diluent used in this method shall be gasoline free from water. When subjected to distillation (see below) it shall show 5 per cent. at a temperature not above 212° F. (100° C.) nor below 194° F. (90° C.). It shall show 90 per cent. at a temperature not above 410° F. (205° C.).

DISTILLATION.

APPARATUS.

DISTILLATION.—*Apparatus.* The Standard Apparatus shall comply with the following specification.

Flask.—The standard 100 c.c. Engler flask is shown in Fig. 40, the dimensions and allowable tolerance being as follows:

	Centimetres.	*Tolerances in Centimetres.*
Diameter of bulb, outside	6·5	0·20
„ „ neck, inside	1·6	0·10
Length of neck	15·0	0·40
„ „ vapour tube	10·0	0·30
Diameter of vapour tube—		
Outside	0·6	0·05
Inside	0·4	0·05
Thickness of vapour tube wall	0·1	0·05

The position of the vapour tube shall be 9 cm. (3·55 inches) ± 3 mm. above the surface of the liquid when the flask contains its charge of 100 c.c. The tube is approximately in the middle of the neck and set at an angle of 75 degrees (tolerance ± 3 degrees) with the vertical.

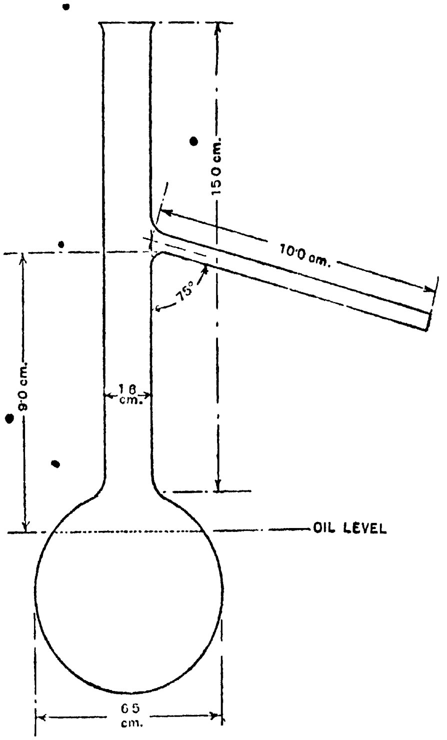


FIG. 40.—STANDARD DISTILLATION FLASK.

Condenser.—The condenser shall consist of a uniform glass 56 cm. (22 inches) in length and 1·25 cm. (± 2 mm.) (½ inch) internal diameter. The lower end of the tube shall be attached to an adapter or bent downwards so that its lowest point may touch the side of the receiving vessel. The condenser shall be cooled by an outer water jacket 38 to 40 cm. (15 inches) in length, through which tap water flows.

Shield and Support.—The flask shall stand in a vertical position on a sheet of asbestos 6 inches square, in the centre of which is a circular hole 1¼ inches in diameter. The flask, support and source of heat shall be surrounded by an efficient screen to eliminate the disturbing effects of draughts.

THERMOMETER SPECIFICATION.

Type.—Mercury in glass. Solid stem. Nitrogen filled.

Stem.—Lead glass or other suitable glass. Enamel back. Diameter, 5·5 to 7 mm.

Bulb.—Cylindrical. Powell's normal glass, Jena 16^{111}, or other approved glass. Length, 10 to 15 mm. Diameter, less than stem.

Range.—0° to 300° C.

Immersion.—Total.

Dimensions.—Overall length approximately 380 mm. The distance from the bottom of the bulb to the 35° mark shall not be less than 110 mm. or more than 135 mm. The total length of the graduated portion shall be not less than 210 mm. or more than 250 mm.

Expansion Chamber.—Required.

Graduation.—The scale divided to 1° C. divisions. Every 5° and 10° shall be indicated by longer lines.

Figuring.—The scale shall be figured at each 10°.

Marking.—" I.P.T. Low Distillation." Identification number. Maker's (or vendor's) name or trade mark.

Each thermometer shall be tested at the National

Physical Laboratory, where satisfactory thermometers will be marked with the N.P.L. monogram and year of test, and a certificate of corrections issued.

Graduated Receiver.—The graduate shall be of the cylindrical type, of uniform diameter, with a pressed or moulded base and a lipped top. The cylinder shall be graduated to contain 100 c.c., and the graduated portion shall be not less than 18 cm. (7 inches), and not more than 20 cm. (8 inches) long. It shall be graduated in single cubic centimetres, and each fifth mark shall be distinguished by a longer line. It shall be numbered from the bottom up at intervals of 10 c.c. The distance from the 100 c.c. mark to the rim shall be not less than 3 cm. (1¼ inches), nor more than 4·5 cm. (1¾ inches). The receiver shall comply with the accuracy requirements of the National Physical Laboratory for Class B graduated glassware.

METHOD.

The flask shall be clean and dry. The condenser shall be rinsed with a little of the liquid under test and allowed to drain for three minutes. One hundred c.c. of the liquid to be tested shall be measured in the graduated jar and transferred to the flask, special care being taken that the side arm of the flask is not wetted. The graduated jar shall be used without drying, as receiver.

The thermometer, the bulb of which shall be covered with a fresh uniform layer of cotton-wool, 5 mgs. in weight, shall be inserted in the flask so that the lower end of the capillary is level with the lower edge of the side arm at its point of attachment to the flask.

The flask shall be attached to the condenser so that the end of the side arm is central in the condenser tube and projects 2·5 cm. beyond the cork. The end of the condenser or adapter shall touch the side of the receiver, the open mouth of which shall be covered with wet filter paper.

The preliminary period between starting the heating and the appearance of first drop shall be a minimum of five minutes, and shall not exceed ten minutes.

The flame shall be set at a size to give a rate of distillation of 4 to 5 c.c. per minute (approximately 2 drops per second), and suitably increased up to 90 per cent. off; then left at this size till the final boiling-point is reached. The initial boiling-point shall be the temperature recorded when the first drop of liquid falls from the side arm of the flask, and the final boiling-point the temperature recorded when the bottom of the flask becomes dry.

The condenser shall be allowed to drain for 3 minutes before measurement of total distillate.

Measurements to be recorded.

I.B.P. AND F.B.P. (RECOMMENDED TOLERANCE OF 5° C.).

Distillate at 150° C.	Distillate at 150° C.
,, ,, 75° C.	,, ,, 175° C.
,, ,, 100° C.	,, ,, 200° C.
,, ,, 125° C.	,, ,, 225° C.

Total distillate. Residue in flask. Loss. Barometer pressure.

No corrections for barometric pressure nor for exposed thermometer stem shall be applied.

LOSS ON HEATING.

I.P.T. Serial Designation—A. 17.
A.S.T.M. Serial Designation—D 6—20.

1. This test is used to determine the loss in weight (exclusive of water) of oil and asphaltic compounds when heated as hereinafter prescribed. The material under examination must therefore first be tested for water, and if water is found to be present it must be removed by suitable methods of dehydration before the material is subjected to the loss on heating test; or another sample obtained which is free from water.

APPARATUS (FIG. 4).

2. The oven may be either circular or rectangular in form and may be heated by either gas or electricity. Its interior dimensions shall be as follows: Height, not less than 40·5 cm. (16 inches); width and depth or diameter, at least 4 cm. (1⅝ inches) greater than the diameter of the revolving shelf.

It shall be well ventilated and shall be fitted with a window in the upper half of the door, so placed and of sufficient size to permit the accurate reading of the thermometer without opening the door. It shall also be provided with a perforated circular shelf preferably of approximately 25 cm. (9¾ inches) in diameter. This shelf shall be placed in the centre of the oven and shall be suspended by a vertical shaft and provided with mechanical means for rotating it at the rate of 5 to 6 revolutions per minute. It shall be provided with recesses equidistant from the central shaft in which the tins containing the samples are to be placed. (A recommended form of aluminium shelf is shown in Fig. 4.)

THERMOMETER SPECIFICATION.

Type.—Mercury in glass. Solid stem. Nitrogen filled.

Stem.—Lead glass or other suitable glass. Enamel back.

Bulb.—Cylindrical. Powell's normal glass, Jena 16^{III}, or other approved glass. Length 10 to 15 mm.

Range.—150° to 175° C.

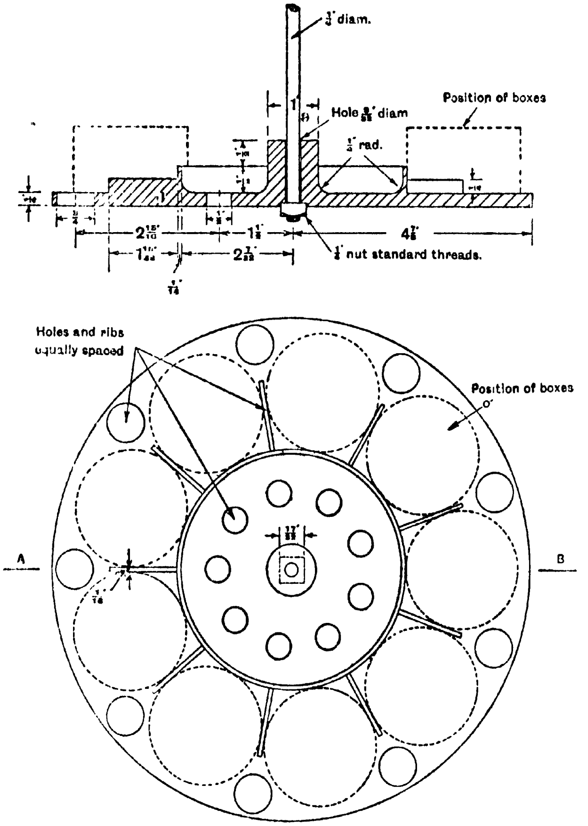
Immersion.—Total.

Dimensions.—Overall length, 130 to 150 mm. Distance from bottom of bulb to first graduation mark approximately 50 to 55 mm.

Expansion Chamber.—Required.

Finish.—Glass ring.

Graduation.—Every 0·5 degree. Each degree larger than the ½ degree and each 5° and 10° shall be indicated by larger lines than the degrees. The 0·5 degree division shall be approximately 1·5 mm.



PLAN.

Fig. 41.—Aluminium Shelf for Asphalt Samples.

Figuring.—The scale shall be figured at each 5°.

Marking.—" I.P.T. Asphalt. A. 17." Identification number. Maker's (or vendor's) name or trade mark.

Each thermometer shall be tested at the National Physical Laboratory, where satisfactory thermometers will be marked with the N.P.L. monogram and year of test, and a certificate of corrections issued.

4. The container in which the sample is to be tested shall be of tin or aluminium, cylindrical in shape, and shall have a flat bottom. Its inside dimensions shall be substantially as follows:—Diameter 55 mm. (2·2 inches), depth 35 mm. (1·4 inches).

PREPARATION OF SAMPLE.

5. The sample as received shall be thoroughly stirred and agitated, warming, if necessary, to insure a complete mixture before the portion for analysis is removed.

METHOD.

6. Fifty grams of the water-free material shall be weighed into a tared container conforming to the requirements of section 4 (above). The oven shall be heated to a temperature of 163° C. (325° F.), and the tin box containing the sample placed in one of the recesses of the revolving shelf. The thermometer shall be immersed for the depth of its bulb in a separate 50-gram sample of the material under test, placed in a similar container, and shall be conveniently suspended from the vertical shaft. This sample shall rest in one of the recesses upon the same shelf and revolve with the sample or samples under test. The oven shall be closed and the shelf rotated 5 to 6 revolutions per minute during the entire test. The temperature shall be maintained at 163° C. (325° F.) for 5 hours, then the sample shall be removed from the

oven, cooled and weighed, and the loss due to volatilisation calculated.

7. During the 5-hour period the temperature shall not vary more than 1° C. All tests showing a greater variation in temperature shall be rejected.

ACCURACY.

8. Up to 5 per cent. loss in weight the results obtained may be considered as correct within 0·5. Above 5 per cent. loss in weight the numerical limit of error increases 0·01 for every 0·5 per cent. increase in loss by volatilisation as follows:

Volatilisation Loss (per Cent.).	*Numerical Correction.*	*True Volatilisation Loss (per Cent.).*
5·0	± 0·5	4·5 to 5·5
5·5	± 0·5	5·0 „ 6·0
6·0	± 0·5	5·5 „ 6·5
10·0	± 0·6	9·4 „ 10·6
15·0	± 0·7	14·3 „ 15·7
25·0	± 0·9	24·1 „ 25·9
40·0	± 1·2	38·8 „ 41·2

PRECAUTIONS.

9. Under ordinary circumstances a number of samples having about the same degree of volatility may be tested at the same time. Samples varying greatly in volatility should be tested separately. Where extreme accuracy is required not more than one material should be tested at one time, and duplicate samples of it should be placed simultaneously in the oven. Such duplicates shall check within the limits of accuracy given above. Results obtained on samples showing evidences of foaming during the test shall be rejected.

NOTE.—If additional periods of heating are desired, it is recommended that they be made in successive increments of 5 hours each.

When the penetration of the sample after heating is required, the residue in the container shall be melted at the lowest possible temperature and thoroughly mixed by stirring, taking care to avoid incorporating air bubbles in the mass. It shall then be brought to the standard temperature and tested as prescribed under the directions for the Standard Test for Penetration of Bituminous Materials.

PENETRATION.

I.P.T. Serial Designation—A. 18.
A.S.T.M. Serial Designation—D 5—21.

DEFINITION.

1. Penetration is defined as the consistency of a bituminous material, expressed as the distance that a standard needle vertically penetrates a sample of the material under known conditions of loading, time and temperature. Where the conditions of test are not specifically mentioned, the load, time and temperature are understood to be 100 grams, 5 seconds, 25° C. (77° F.), respectively, and the units of penetration to indicate hundredths of a centimetre.

APPARATUS.

2. The container for holding the material to be tested shall be a flat-bottom, cylindrical dish, 55 mm. ($2\frac{3}{16}$ inches) in diameter and 35 mm. ($1\frac{3}{8}$ inches) deep.

The needle for this test (Fig. 42) shall be a cylindrical steel rod 50·8 mm. (2 inches) long, having a diameter of 1·01 to 1·02 mm. and having a taper of 6·34 to 6·36 mm. measured on the axis. After tapering, the point shall be "blunted" by grinding off to a truncated cone, the smaller base of which shall be from 0·14 to 0·16 mm.

in diameter. The penetration needle shall be gauged for dimensions by the National Physical Laboratory.

The water-bath shall be maintained at a temperature not varying more than 0·1° C. from 25° C. (77° F.). The volume of water shall be not less than 10 litres, and the sample shall be immersed to a depth of not less than 10 cm. (4 inches), and shall be supported on a perforated shelf not less than 5 cm. (2 inches) from the bottom of the bath.

Any apparatus which will allow the needle to penetrate without appreciable friction, and which is accurately calibrated to yield results in accordance with the definition of penetration, will be acceptable.

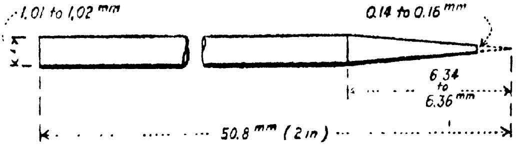


FIG. 42.—NEEDLE FOR PENETRATION TEST.

The transfer dish for container shall be a small dish or tray of such capacity as will insure complete immersion of the container during the test. It shall be provided with some means which will insure a firm bearing and prevent rocking of the container.

PREPARATION OF THE SAMPLE.

3. The sample shall be completely melted at the lowest possible temperature and stirred thoroughly until it is homogeneous and free from air bubbles. It shall then be poured into the sample container to a depth of not less than 15 mm. ($\frac{5}{8}$ inch). The sample shall be protected from dust and allowed to cool in an atmo-

sphere, not lower than 18° C. (65° F.) for one hour. It shall then be placed in the water-bath along with the transfer dish and allowed to remain one hour.

METHOD.

4. (*a*) In making the test the sample shall be placed in the transfer dish filled with water from the water-bath of sufficient depth to completely cover the container. The transfer dish containing the sample shall then be placed upon the stand of the penetration machine. The needle, loaded with specified weight, shall be adjusted to make contact with the surface of the sample. This may be accomplished by making contact of the actual needle point with its image reflected by the surface of the sample from a properly placed source of light. Either the reading of the dial shall then be noted or the needle brought to zero. The needle is then released for the specified period of time, after which the penetration machine is adjusted to measure the distance penetrated. At least three tests shall be made at points on the surface of the sample not less than 1 cm. (3/8 inch) from the side of the container and not less than 1 cm. (3/8 inch) apart. After each test the sample and transfer dish shall be returned to the water-bath and the needle shall be carefully wiped towards its point with a clean, dry cloth to remove all adhering bitumen. The reported penetration shall not differ more than four points between maximum and minimum.

(*b*) When desirable to vary the temperature, time and weight, and in order to provide for a uniform method of reporting results when variations are made, the samples shall be melted and cooled in air as above directed. They shall then be immersed in water or brine, as the case may require, for one hour at the temperature desired. The following combinations are suggested:

At 0° C. (32° F.), 200 grams weight, 60 seconds.
At 46° C. (115° F.), 50 grams weight, 5 seconds.

DUCTILITY.

I.P.T. Serial Designation—A. 19.

DEFINITION.

Ductility is a test of the consistency of bituminous material, the results of which are expressed in the distance in centimetres that a block of standard shape and dimensions and at a standard temperature can be drawn out before fracture.

APPARATUS.

The standard pattern Dow ductility machine shall be used, with the following modification: The distance between the carrier plate and the bottom of the trough shall be 1 cm.

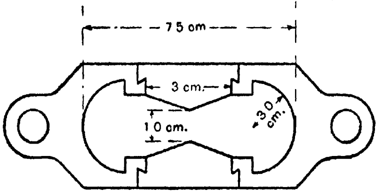


FIG. 43.—MOULD FOR DUCTILITY TEST.

It is further recommended that—

1. The standard instrument shall be mechanically driven, preferably by electrical means.

2. A milk glass sheet be placed at the bottom of the trough so as to present an even surface which will not break the thread of bitumen under test.

3. The moulds have sloping side pieces, so that a slight inward pressure binds the whole mould together.

4. Hot water from a suitable supply or electric heating be used instead of the present practice of heating by gas jets placed beneath the trough.

The dimensions of the mould (Fig. 43) shall be approximately—

	Centimetres.
Internal length	7·5
Distance between ends of clips	3·0
Extreme width	3·0
Internal width, at mouth of clips	2·0
Thickness of sample block	1·0

CONDITIONS FOR TEST.

The water-bath for the samples must be maintained at all depths at a temperature of 15° C. (60° F.), constant to within 0·1° C. The volume of water shall not be less than 10 litres, and the sample shall be immersed to a depth of not less than 10 cm. (4 inches), and shall be supported on a perforated shelf not less than 5 cm. (2 inches) from the bottom of the bath.

PREPARATION OF THE SAMPLE.

A clean representative sample shall be heated, with occasional stirring, in a round-bottom nickel vessel. The quantity must be sufficient for a test in triplicate. Place the dish well above a source of heat, and raise the temperature at such a rate that 130° C. (266° F.) is reached in one hour. If bubbles or froth persist, heat at this temperature for another half-hour. If they are still present, they shall be broken with a tiny gas flame; but if they are not to be driven off, another sample shall be taken for testing.

If the sample is markedly impure, it shall be heated for as short a time as is possible without the risk of overheating at 150° C. (302° F.), and strained through a 50-mesh sieve.

Precautions.—It is essential that all heating of the bitumen shall be at as low a temperature and as slow a rate as is practicable, and at the same time in accordance with the above instructions.

The base-plate and the side pieces of three brass moulds shall be amalgamated with mercury. The parts of the moulds shall be assembled on their plates and the melted sample poured almost to overflowing. A warmed strip of amalgamated brass plate shall be pressed over the central portion to level the sample, and the ends levelled with a warmed sharp knife only.

The poured samples shall cool for one hour in air, protected from dust, and for one and a half hours in water at the temperature of the test.

METHOD.

The temperature of the water in the trough of the ductility machine shall be raised to that desired, normally 15·5° C., and the heating arrangements adjusted so that it remains constant. The side pieces of the moulds shall be removed and the samples transferred from their base plates to their positions in the machine. The carriage shall be set in motion at the standard speed of 5 cm. per minute, and the distance travelled when each thread breaks noted. The highest of these figures shall be reported.

When it is required to examine more broadly the general characteristics of a sample, tests may be made at other temperatures, those suggested being 20° C. and 25° C.

Tolerance.—5 per cent.

SOFTENING-POINT (RING-AND-BALL METHOD).

I.P.T. Serial Designation—A. 20.
A.S.T.M. Serial Designation—D 36—21.

DEFINITION.

1. The softening of bituminous materials generally takes place at no definite moment or temperature. As the temperature rises, they gradually and imperceptibly change from a brittle or exceedingly thick and slow flowing material to a softer and less viscous liquid. For this reason the determination of the softening-point must be made by a fixed, arbitrary and closely defined method if the results obtained are to be comparable.

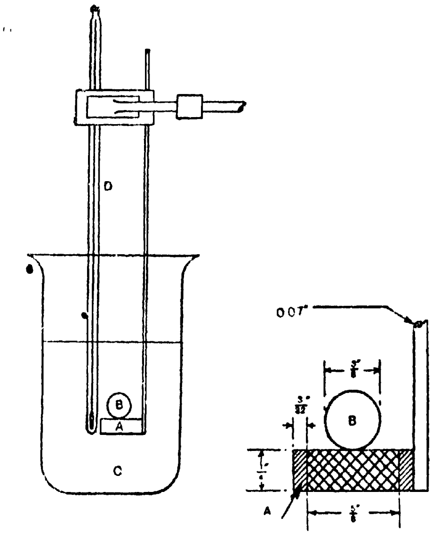


FIG. 44.—RING-AND-BALL APPARATUS FOR SOFTENING POINT.

APPARATUS (FIG. 44).

2. The apparatus shall consist of the following:

A. A brass ring 15·875 mm. ($\frac{5}{8}$ inch) in inside diameter and 6·35 mm. ($\frac{1}{4}$ inch) deep; thickness of wall, 2·38 mm. ($\frac{3}{32}$ inch); permissible variation on inside diameter and thickness of ring, ± 0·25 mm. (0·01 inch). This ring shall be attached in a convenient manner to a No. 15 S.W.G. brass wire, diameter 1·83 mm. (0·072 inch). (See Fig. 7.)

B. A steel ball 9·53 mm. ($\frac{3}{8}$ inch) in diameter weighing between 3·45 and 3·55 grams. A ball-bearing ball invariably conforms with the requirements.

C. A glass vessel, capable of being heated, not less than 8·5 cm. (3·3 inches) in diameter and measuring 10·5 cm. (4 inches) in depth from the bottom of the flare. (A 600 c.c. beaker, low form, meets this requirement.)

THERMOMETER SPECIFICATIONS.

Type.—Mercury in glass. Solid stem.

Stem.—Lead or other suitable glass. Enamel back. Diameter 6·5 to 7·5 mm.

Bulb.—Cylindrical. Powell's normal glass. Jena 16,^{111} or other approved glass. Length, not over 14 mm. Diameter, 4·5 to 5·5 mm.

Range.—0° to 80° C. (32 to 176° F.).

Immersion.—Total.

Dimensions.—Total length, 370 to 400 mm. The distance from the bottom of the bulb to the first scale division shall not be less than 75 mm. The distance from the 0° mark to the 80° mark shall be between 230 and 275 mm.

Expansion Chamber.—Required.

Finish.—Glass ring.

Graduation.—0·5° division for C. or F. scale. Each degree longer than the half-degrees, and each 5° and 10° shall be indicated by longer lines than the degrees.

Figuring.—The scale shall be figured at each 5° or 10°.

Marking.—"I.P.T. A20." Identification number. Maker's (or vendor's) name or trade mark.

Each thermometer shall be tested at the National Physical Laboratory, where satisfactory thermometers will be marked with the N.P.L. monogram and year of test, and a certificate of corrections issued.

PREPARATION OF SAMPLE.

3. The sample shall be melted and stirred thoroughly, avoiding incorporating air bubbles in the mass, and then poured into the ring so as to leave an excess on cooling. The ring, while being filled, should rest on a brass plate which has been amalgamated to prevent the bituminous material from adhering to it. After cooling, the excess material shall be cut off cleanly with a slightly heated knife.

METHOD.

(*A*) *Bituminous Materials having Softening-Points* 80° *C.* (176° *F.*) *or below.*

4. The apparatus shall be assembled as shown in Fig. 7, and the glass vessel filled to a depth of 3 to $3\frac{1}{2}$ inches, with freshly boiled, distilled water at 5° C. The ball shall be placed in the centre of the upper surface of the bitumen in the ring, and the ring suspended in the water so that the lower surface of the filled ring is exactly 1 inch above the bottom of the glass vessel and its upper surface is 2 inches below the surface of the water. It shall remain in the water for 15 minutes before applying heat. The thermometer shall be suspended so that the bottom

of the bulb is level with the bottom of the ring and within ¼ inch, but not touching the ring.

5. Heat shall be applied in such a manner that the temperature of the water is raised 5° C. (9° F.) each minute.

6. The temperature recorded by the thermometer at the instant the bituminous material touches the bottom of the glass vessel shall be reported as the softening-point.

7. The rate of rise of temperature shall be uniform and shall not be averaged over the period of the test. The maximum permissible variation for any minute period after the first three shall be ± 0·5° C. (0·9° F.). All tests in which the rate of rise in temperature exceeds these limits shall be rejected.

(*B*) *Bituminous Materials having Softening-Points above 80° C. (176° F.).*

8. The same method as given under (*A*) shall be used, except that glycerin shall be used instead of water, that the initial temperature shall be 30° C., and that the thermometer shall conform to the following specifications:

THERMOMETER SPECIFICATIONS.

Type.—Mercury in glass. Solid stem. Nitrogen filled.

Stem.—Lead or other suitable glass. Enamel back. Diameter 6·5 to 7·5 mm.

Bulb.—Cylindrical. Powell's normal glass, Jena 16,[111] or other approved glass. Length not over 14 mm. Diameter, 4·5 to 5·5 mm.

Range.—30° to 160° C.

Immersion.—Total.

Dimensions.—Total length, 370 to 400 mm. Distance from the bottom of the bulb to 30° mark not less than 75 mm. Distance from 30° mark to 160° mark shall be between 230 and 275 mm.

Expansion Chamber.—Required.

Finish.—Glass ring.

Graduation.—0·5° divisions. Each degree larger than the half-degrees, and each 5° and 10° shall be indicated by longer lines than the degrees.

Figuring.—The scale shall be figured at each 10°.

Marking.—" I.P.T. A20." Identification number. Maker's (or vendor's) name or trade mark.

Each thermometer shall be tested at the National Physical Laboratory, where satisfactory thermometers will be marked with the N.P.L. monogram and year of test, and a certificate of corrections issued.

PRECAUTIONS.

9. The use of freshly boiled distilled water is essential, as otherwise air bubbles may form on the specimen and affect the accuracy of the results. Rigid adherence to the prescribed rate of heating is absolutely essential in order to secure accuracy of results.

A sheet of paper placed on the bottom of the glass vessel and conveniently weighted will prevent the bituminous material from sticking to the glass vessel, thereby saving considerable time and trouble in cleaning.

ACCURACY.

10. The limit of accuracy of the test is ± 0·5° C. (0·9° F.).

WAX IN ASPHALT.

I.P.T. Serial Designation—A. 31.

METHOD.

From 1 to 3 grams of the sample (according to the amount of suspected wax) shall be weighed into an evaporating basin of about 200 c.c. capacity, approximately 10 times the weight of pure concentrated sulphuric acid added, and the basin and contents warmed on a sand-bath.

When the bitumen shows signs of melting the mixture shall be stirred at intervals. Frothing occurs and sulphur dioxide is given off, and the bitumen assumes a porous spongy carbonaceous mass. This should occur in from 15 to 20 minutes and overheating shall be avoided.

The basin and contents shall be allowed to cool. The bitumen should now have the appearance of a dry soft coke.

The carbonaceous mass shall be broken up roughly with a glass rod and 50 to 100 c.c. of water added and sufficient solid sodium carbonate to make the whole distinctly alkaline.

The contents shall be filtered through a Buchner funnel and the charred mass washed once or twice with water.

The bulk of the char shall be removed and roughly crushed in a mortar, and the crushed mass, the filter paper and the small piece of cotton-wool used to wipe out the mortar transferred to a flask (a 200 c.c. conical for preference), and the flask fitted with a reflux condenser.

Fifty c.c. of a mixture of ethyl ether and alcohol, equal parts, shall be poured through the condenser, and the mixture allowed to boil gently for 15 minutes.

The contents whilst still hot shall be poured through a funnel containing a pledget of cotton-wool into a beaker standing in a basin of iced water.

The extraction shall be repeated twice more with fresh quantities of ether/alcohol, filtering these extracts whilst hot through the same cotton-wool into the same beaker.

The wax rapidly separates out in flakes, the beaker being finally cooled by standing it in icesalt mixture.

A Gooch crucible shall be prepared with asbestos in the usual way, dried and weighed, and attached to the filter pump. Pour through the Gooch a few c.cs of alcohol/ether, which has been cooled in ice/salt, then, with the vacuum slightly on, the cold wax suspension shall be added. The large bulk of cold alcohol/ether prevents undue heating during the short time of filtering.

The mass shall be washed once with cold ether/alcohol and the Gooch and its contents dried in the oven on a weighed watch glass for two hours, the Gooch crucible for preference lying on its side.

The Gooch and its contents shall be cooled, weighed, and the percentage of wax in the sample calculated.

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CHAPTER II

THE COMPOSITION AND ORIGIN

General Nature

The difficulties associated with the detailed investigation of the constituents of bituminous substances and the establishment of their identity and constitution have been so great as to be baffling to a considerable degree. To the same extent a definite pronouncement as to the origin of these substances is not possible, and this is being delayed until just that moment when analysis becomes capable of "pulling its weight" in the elucidation of the problem. So far successful investigation of these substances[30-36, 28] has resulted only in establishing the existence of groups of compounds of high molecular weight, the presence and proportion of combined oxygen, sulphur and nitrogen, and some evidence as to the degree of saturation of the component substances. The presence has also been substantiated of aliphatic and cyclic hydrocarbons, of which the most important are the naphthenes, polynaphthenes, naphthylenes and terpenes, together with condensed substances, resulting from these by oxidation, thionisation and polymerisation. By selective solution there have been established—

Malthenes, soluble in carbon disulphide and in light petroleum naphtha.

Asphaltenes (and resins), soluble in carbon disulphide and insoluble in light petroleum naphtha.

Carbenes, soluble in carbon disulphide and insoluble in carbon tetrachloride.

Carboids, insoluble in carbon disulphide or other organic liquids.

This classification is very useful for identification by the proportions in which these groups of compounds are present, as will be seen in Table I.

TABLE I.

CLASSIFICATION OF BITUMINOUS CONSTITUENTS.

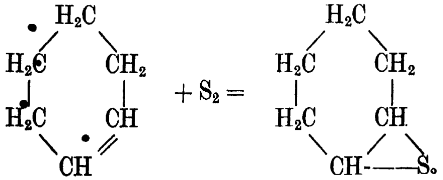
	Asphaltenes (Per Cent.).	*Carbenes (Per Cent.).*	*Kerotenes (Per Cent.).*
Asphaltic petroleum	0 to 10	0 to 1	0 to 2
Gilsonite	40 „ 60	0 „ ½	0 „ 2
Glance-pitch ..	30 „ 50	<1	<1
Grahamite	trace to 50	0 „ 80	<5
Albertite	up to 20	0 „ 2	90 to 98
Wurtzilite	up to 20	0 „ 2	90 „ 95

However, to obtain greater insight into the nature of the various materials a closer examination must be made. This has been effected by chemical methods,[30, 35] whereby the following groups of substances are recognised:

(*a*) Neutral petroleum resins.
(*b*) Asphaltenes.
(*c*) Asphaltogenic acids and anhydrides.

The *asphaltenes and resins* are saturated polycyclic bodies containing oxygen or sulphur. Both of these elements can exist in ring formation; the latter exist also in the form of sulphide or thio-ether. The formation of these compounds is doubtless along the following lines. From unsaturated naphthylenes and terpenes:

1.



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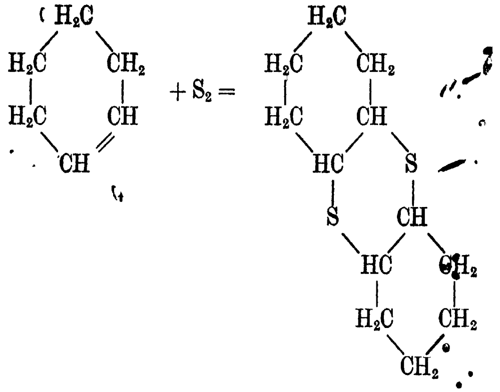
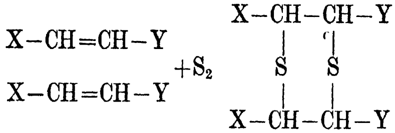


and from fatty acid decomposition products:



$$\begin{array}{l} X-CH=CH-Y \\ X-CH=CH-Y \end{array} + S_2 \quad \begin{array}{c} X-CH-CH-Y \\ \quad\ |\qquad\ | \\ \quad\ S\qquad S \\ \quad\ |\qquad\ | \\ X-CH-CH-Y \end{array}$$

A further possible change is the condensation of two molecules of a sulphide with elimination of sulphuretted hydrogen.

The action of oxygen has not been so exactly described, but its effect has been measured.[37] Air passed through a Weitzer crude oil at 120-130° and 170° raised the asphaltenes from 17·5 per cent. to 35 and 42·5 per cent., with simultaneous and almost complete conversion of the resins into these bodies. The change is based primarily on the oxidation and polymerisation of unsaturated compounds and sulphur-containing rings. In this case, asphaltogenic acids were not formed in appreciable quantities.

Asphaltogenic acids have been studied to a considerable extent, as their preparation in the laboratory is not difficult. They are formed, together with naphthenic acids, when air acts on heated heavy oils, and the reaction is assisted by the presence of alkalis. Both groups of substances are soluble in carbon disulphide, chloroform, alcohol, ether and benzene; but the asphaltogenic acids are separated by their own insolubility in petroleum ether, and that of their copper salts in hydrocarbons. They are brownish-black, thick substances, unstable, and easily resinified by heat or strong alkalis. They probably consist of dimolecular dihydroxy-monocarboxylic acids, $C_{20}H_{25}O_4$, in which the two alcoholic groups cause behaviour as of a pseudo-acid. Aldehidic reactions are observed, but the characteristic grouping has not been found. They contain no sulphur that can be eliminated by alcoholic potassium hydroxide. The alkali salts are soluble in water, but the sodium salt dissolves with difficulty in aqueous alkali. Prolonged heating at 120° C. caused the formation of anhydrides; whilst at a higher temperature carbon dioxide is eliminated and neutral, unsaponifiable asphaltenes are formed.

It is possible that the nitrogen that is found to be present in this mixture exists in an interesting form. In order to test the hypothesis that it exists as a salt-like compound of a highly complex acid with an equally complex nitrogen base, artificially prepared asphaltogenic acid was combined with a molecular quantity of pyridine, and of other bases. The resulting compound was brittle, pitch-like, resinous and brilliant in appearance, and melted with difficulty, a description which might be applied to certain characteristic bituminous materials.

The *oily constituents* show all the characteristics of normal thick, fluorescent mineral oils, and are dextrorotatory to polarised light. They are mainly a mixture of saturated and unsaturated substances; the former consist mainly of naphthenes and polynaphthenes, and the latter are shown also to be cyclic by giving the formolite reaction. This oil also contains oxygen, sulphur, and nitrogen compounds, but in small quantities, together with, characteristically, paraffin wax. Sulphuric acid removes the resins that are present and converts the thick oil into a liquid resembling machine oil.

Petroleum distillation residues contain practically no asphaltogenic acids and less asphaltenes than does the naturally occurring material, but their composition, and that of the associated resins, is the same. The oily constituents are higher in proportion, and the action of sulphuric acid on them has no effect on the consistency of the oil.

The most intimate chemical study of the "petrolites" and their relations to the paraffin series of compounds has been published by Hackford.[38]

Most characteristic for the asphaltic oils is the presence of asphaltenes; most characteristic for the paraffin type of oil is paraffin wax; and these can be chemically connected under quite simple conditions of change—relations which are, perhaps, best indicated by simple statements.

Thio-ceresine in Mexican bitumen when heated loses sulphuretted hydrogen and becomes converted into paraffin wax.

$$\begin{tikzcd}
 & \text{oil and wax} & \\
\text{Diasphaltenes} \arrow[r, "\text{gentle}", "\text{heat}"'] & \text{Asphaltenes} \arrow[u, "\text{dist.}"] \arrow[r, "\text{gentle}", "\text{heat}"'] & \text{Kerols (insol.}
\end{tikzcd}$$

$$\begin{tikzcd}
\text{oil and wax} & \text{oil and wax} & \\
CS_2,\ \text{sol.}\ CHCl_3) \arrow[u, "\text{dist.}"] \arrow[r, "\text{gentle}", "\text{heat}"'] & \text{Keroles (insol.}\ CHCl_3) \arrow[u, "\text{dist.}"] \arrow[r, "\text{gentle}", "\text{heat}"'] & {}
\end{tikzcd}$$

a substance insoluble in all known solvents. These changes have been brought about in two months at a temperature of 80°-100° C.

Yet, in spite of this close intimacy, a material fluxed with a paraffin base oil will show a consistency quite different from that of a sample of the same material fluxed with an asphaltic base oil.[39]

As clear an idea as is possible at present will have been gained as to the general nature of these substances, so that their mode of formation can now be discussed.

MODE OF FORMATION.

It is remarkable that even at this late date a *cosmic* theory[40] for the origin of naturally occurring combustible matter should be put forward. It is suggested that the elements carbon, hydrogen, nitrogen and sulphur which existed free—on account of the high temperature—in the nebula from which resulted the solar system, combined together when the temperature had fallen to a suitable degree to permit of the formation of the simpler organic compounds. More complex substances were formed on further cooling, and anthracite, coal, bitumen, petroleum and gas resulted according to the conditions of temperature, pressure, oxidation, thionisation, decomposition and polymerisation.

Although such ideas do not carry weight, serious attention has been given to the presence of bitumen in meteorites, a widely repeated statement which will be seen to have no real foundation.

Examination has been made[41-45] of the alcohol- and ether-soluble material of a number of meteorites that have fallen in France, Hungary, America and elsewhere, mainly between the years 1834 and 1888; no recent work seems to have been done on the subject. The solid residue left after evaporisation of the solvent consisted of (*a*) a hydrocarbon, crystallising in acicular form, m.p. 114° or 120°, in quantity less than 1 per cent. of the total weight of the meteorite; (*b*) some free sulphur; and (*c*) graphite. The quantities obtained were so small that quantitative analysis could give only approximate results, so that the suggestion of the existence of a compound $C_4H_{12}S_5$ is scarcely to be credited without further substantiation. (See also [186-188].)

It can, however, be clearly seen that the mixture is not "bitumen," but its presence is intriguing, considering that, whilst being easily destroyed by heat, it is discovered within a mass that has clearly been heated to a very high temperature. It appears to the writer that the hydrocarbon has resulted by the action of terrestrial water on carbides within the meteorite after its arrival on the earth. This theory is supported by a number of facts. Iron-nickel carbide is frequently present in meteorites. Solid hydrocarbons, however, result from the action of water on carbides of the higher-valency metals. These can be present in small quantities, but not often; this hydrocarbon is found in small quantities, but not often. Water when poured on to a powdered sample of a meteorite was found to cause an "alliaceous" odour; this is doubtless assisted by the decomposition of phosphide which has also been identified (the basic nitrogen that has been obtained might come from a nitride). The water found in meteorites is considered by authorities not to be original, but to have been taken up at some later period.[46] Very significantly, it has been found that the soluble matter can be completely removed from the bulk of the meteorite without any pulverisation,[47] from which it would seem that it had been formed in the cracks and pores, just the positions into which water could percolate (See also [66].)

There exists no doubt that the bitumens and asphaltites are very intimately connected with petroleum, but there is some uncertainty as to which was formed first. It is usually assumed that the various substances constitute successive stages which the action of oxygen or sulphur has produced in petroleum, by causing, not merely oxidation and thionisation, but also associated condensation and polymerisation—a change which, most curiously, can be accelerated by "seeding"; and further, sulphur has been considered to act as a dehydrogenating agent, and to cause the formation of unsaturated substances.[31]

The hardening action of sulphur is undoubted, and such "vulcanisation" is employed to harden a bitumen for purposes of insulation, waterproofing, etc.[48]

An interesting observation was made that seems to show that sulphur is largely a promoter of change rather than an active chemical agent. It was found that oils oxidised more rapidly when containing their natural sulphur compounds than after desulphurisation; also, that passage of air in presence of sulphur caused oxidation, but passage of natural gas in presence of sulphur did not lead to thionisation. Possibly the first action was for the sulphur to combine with the olefine compounds to form saturated compounds which subsequently lost sulphuretted hydrogen; then oxygen acted and caused polymerisation.

The access of external sulphur is clear from the fact that crude petroleum contains 0·01 to 2·2 per cent., whilst the content in bitumen is usually 2 to 12 per cent. That this increase is not due to simple concentration of sulphur-containing bodies is the more likely as sulphur and sulphides and potential sulphides in the form of sulphate accompany oil and bitumen. These are usually derived from gypsum in the associated waters, which is reduced by organic matter to calcium sulphide with the formation of carbon dioxide, which at once reacts to form calcium carbonate and sulphuretted hydrogen. Or the calcium sulphide may exchange sulphur in return for oxygen.

When, however, no sulphur has been present, oxydation and polymerisation have been responsible for the changes, and then the oxy-asphaltites are formed.

It is in this manner that it is generally considered that oil is converted into the malthene, asphalt, carbenes,[49] (contained in) bitumen, and subsequently into the asphaltites and "kerites" with increasing insolubility in the usual solvents, including acetone.[50]

The basis of these assumptions is not only on analytical grounds, but also on the reproduction in the laboratory of something very like bitumen by the same reactions.[51] The changes have been studied in Russian (Baku) oil, in order to produce a commercially useful substance. Oxygen behaved as it was expected to do (see also "Asphaltogenic Acids," p. 14), but it is interesting to note that at 300° to 320 ° C. the reaction was exothermic. With regard to sulphur (see also "Asphaltenes," p. 13) reaction proceeds, but with the evolution of sulphuretted, hydrogen at 190° to 250° C.

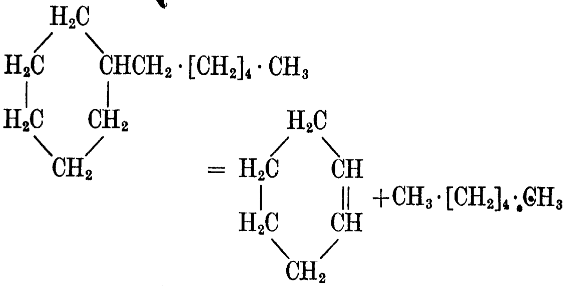
There is, therefore, much in favour of accepting this theory of the conversion of petroleum first into bitumen, and subsequently into the asphaltites and then the "kerites."

An experiment of exposing various bituminous substances to light and air for a year showed that the changes that occurred in these circumstances also were in the same direction. It was found that the material insoluble in benzole increased 0 to 6 times, and that that insoluble in carbon tetrachloride (carbenes) increased somewhat; fixed carbon rose about 2 per cent.; the melting-point increased appreciably and the penetration went down by one-half to one-third.[52] It had previously been observed that daylight increased the rate of the change, and that radium had no effect.[53]

It is of interest, in the examination of the materials of various geological ages,[18] that the greater the antiquity the lower is the oxygen content, whilst the proportion of carbon is approximately constant. It may be that the oxygen has been used up to change the still unaltered constituents of the mother substance, or to the actual formation of bitumen itself and of its associates. A parallel change, more striking but less obvious as to its mechanism, is the diminution of the relative amount of nitrogen.

It is well known that chemical reactions may be assisted catalytically by the presence of unsaturated materials that act as oxygen-carriers. Experiments have been made of treating different qualities and quantities of petroleum from Central Galicia, under various conditions of heat, pressure and illumination, with a number of condensing agents,[54] of which many (or their nearly related compounds) might be met in the earth by a body of migrating oil. The substances tried were: sodium, sodium sulphide, sodium carbonate, sodium ethylate, sulphur, barium sulphide, barium peroxide, phosphorus, phosphorus pentoxide, cuprous chloride, cobalt chloride, zinc chloride, ferric chloride, aluminium chloride and manganese dioxide; the most active agents being phosphorus pentoxide and aluminium chloride. Ten per cent. of aluminium chloride dissolves in petroleum,[55] and, on distillation, gives a light fraction, gradually increasing in density and having all the properties of light naphtha, together with a heavy portion, which contains all the catalyst.

This shows that the action of aluminium chloride is very deep-seated, causing a separation of hydrocarbon chains and a condensation of them and of their residues, the initial stage of the reaction being:



Dodecanaphthene Hexane

The quantity of the fraction depends on the nature and provenance of the oil. The residue can be freed from the catalyst by washing with hot water or by sublimation in a current of chlorine. According to the nature of the oil, it may be a compact black mass, dull, of conchoidal fracture, and fusible in hot water; or a greyish-black powder, friable and shiny, which does not fuse on the water bath. The latter substance, obtained from a Baku oil, is partially soluble in alcohol, ether, benzene and petroleum ether, and completely so in chloroform; slightly acid potassium permanganate is instantly decolorised in the cold. It is very like the natural bitumens, having a composition C_nH_n, and a decomposition temperature above 200° C.

The most acceptable theory[56] for the formation of petroleum is the decomposition, under peculiar conditions, of organic matter by the action of micro-organisms.

It has further been found recently[57] that certain other commonly occurring bacteria will act on petroleum itself, and will not only cause a separation of the ring-compounds from the aliphatic by destruction of the latter, but also cause the formation of bitumen. If a layer of petroleum, not more than 2 mm. thick, be poured over a mixture of ditch water with a solution of 0·1 per cent. magnesium ammonium phosphate, 0·08 per cent. dipotassium hydrogen phosphate, 0·01 per cent. calcium sulphate, and traces of sodium chloride, potassium iodide and ferric chloride, in a few weeks the oil will have disappeared and the liquid will have become turbid, apparently with bitumen. This might be, in essence, merely an oxidising action, brought about by bacterial agency, since the change will only occur in a very thin layer of the oil; and this is not contradicted by the fact that the same kind of change occurs to a thin slice of paraffin wax when immersed in the solution. It may be argued that ditch water is a reducing medium, but, on the other hand, the nutritive salts can yield oxygen, even if none is obtainable in the upper surface of the liquid.

It seems reasonable to expect that bitumen, in its initial stages of formation in petroleum, would first appear in a very finely divided—colloidal—state. When such an oil rises to the surface of the earth and spreads over it, not only would atmospheric oxidation continuously assist the change, but suspension would be coagulated by the physical effect of light[58] (see also p. 42). This solidified material settling on soil particles would form the nucleus of an asphalt deposit, which would be increased by evaporation of the oil. A secondary effect of light would also occur and cause any dissolved bitumen to become less truly soluble (see "Properties: Action of Light," p. 39).

If, however, bitumen has not been produced subsequently to the formation of petroleum, as some aver, then it must have been produced at an intermediate stage,[27] with petroleum as a final product. This possibility must be considered, but there is little to advance in its favour.

The naturally occurring bituminous substances, particularly those that are found in Russia, on distillation yield a liquid very like the oil found in the Russian oil fields. The deduction is, therefore, that naphtha is formed by the decomposition of bitumen.[59-61]

Further considerations lead to a meeting with another of the many ramifications of the latest development in chemical and physical science—that of colloidal phenomena. The remarkable changes that are associated with extreme subdivision, particularly with those substances that can act catalytically, are found, in high probability, to be happening here. Most striking is the conversion of petroleum into that material known as Trinidad asphalt; for not only is oil converted into bitumen, but the bitumen is also changed into asphalt.[62-65]

This asphalt is a very intimate mixture of bitumen with 27 per cent. mineral matter consisting mainly of clay (containing 4 per cent. of water of hydration), and 29 per cent. of water and gas. The water contains about 2 per cent. of salts, mainly sodium chloride and sulphate, together with ferrous sulphate and amonium sulphate, and small quantities of iodides and borates. The gas contains much sulphuretted hydrogen.

It is considered that in past eras the petroleum, migrating to its present position, came into contact with a mud volcano on the spot of the present asphalt accumulation. The petroleum became emulsified with the mixture of fine silica and clay and water of the mud by the agency of natural gas at high pressures. The clay is finely divided and carries ferrous sulphate adsorbed, which doubtless has acted as a catalyser assisting subsequent change. This mixture, on coming to the surface, hardens, a change partially due, probably, to fall of temperature, but mainly, it would appear, to chemical action.

In the air incomplete oxidation of the sulphuretted hydrogen would probably produce sulphur free to thionise the oil to form bitumen, simultaneously with atmospheric oxygen, acting to form the analogous oxybitumen. However this may be, there has been no general discussion and acceptance of such views.

Such was the state of knowledge until the subject was reviewed and carried considerably further in an important paper by Nellensteyn.[72] He points out, firstly, that bitumen was formed when a Borneo oil of the following constitution was distilled:

D^{15}, 0·9555; C, 87·0; H, 11·0; S, trace, N, 0; O, 0·2 per cent.; therefore sulphur is not a necessity for the change. Then, oxygen occurs with no regularity in the various fractions of distillation, and does not increase with the bitumen content; therefore oxygen is of no essential importance. Also, the relative proportion of hydrogen diminishes with diminishing volatility. Further, distillation is to be looked on as consisting of synthetic and decomposing reactions working in a particular direction, in the sense of Burton's, Bergin's and Trumble's distillations, as compared with the pure physical nature of vacuum distillation.

After a long consideration of other work, particularly of Bone's, Nellensteyn comes to the conclusion that bitumen is formed by the breakdown of carbon chains into very reactive fragments, followed by an oxidising reaction, which does not depend on the oxygen concentration, but on the velocity with which the chains are broken. Thus, there is an immediate connection between the pyrogenic phenomena that are well known, particularly exemplified in hexane which splits off a $-CH_3$ group, and the more recent work on the oxidation of the higher paraffins—both dependent on highly reactive hydrocarbon residues in equilibrium with the parent hydrocarbon.

As a result of the study of the oxidation of the higher paraffins oxygen is found in all the products of reaction—the residue, the distillate and the gases; but in the case of bitumen the distillate is practically oxygen-free. It is of interest to recall here the three main theories: Marcusson's, where the oxygen and sulphur occur in bridge combination; Engler's, where oxygen is merely an aid to polymerisation; and Abraham's, where oxidation leads to dehydrogenation.

Oxidation of an asphaltic oil at 200° to 275° causes the production of formic and acetic acids, water, carbon monoxide and dioxide; at lower temperatures reaction also occurs. The deductions are: oxygen is not exclusively a polymerisation agent; it is not a simple dehydrogenating agent (when water alone should be formed); a high molecular chain is broken down into a polycarbonaceous portion which passes into a stable condition according to known chemical principles, and a single carbon residue which is promptly oxidised.

The oxidation is deep-seated, since CO_2 is always formed; it is incomplete, since CO occurs; it is indirect—that is to say, does not attack the chain directly—since no other oxidation compounds are found.

Thus, the important conclusion is reached that bitumen contains elementary carbon in colloidal form, and that this colloidal carbon is the essential constituent of bitumen. This is fully substantiated by the observation of the Tyndal effect, Brownian movement, and turbidity of extremely dilute benzole solutions. It may here be permitted to interpolate a comment, firstly, that the carbon atom primarily spilt off must retain at first its hydrogen atoms, and that oxidation acts in three ways: the first, where there is complete oxidation as already described; the second, where the carbon atom undergoes a " clean shave " when the amount is exactly enough to remove successively all hydrogen atoms and leave carbon atoms free to come together to particles of colloidal dimensions (see also " Iodine," p. 49); the third, that certain free terminal $-CH_3$ groups escape oxidation for the first instance, unite to form ethane, and are then oxidised to acetic acid.

Turning attention to the asphaltenes, it is observed that they diffuse under conditions of dialysis or ultra-filtration; that they have different chemical compositions, but the same chemical properties.

The colour of colloidal solutions of hydrocarbons is not deep—as, for example, Hevea rubber; that of bitumen solutions is due to elemental carbon.

Change of chemical solubilities is not due to change of chemical composition; the series asphaltenes ——> carbenes ——> " free carbon " is due to the successive removal of non-asphaltic bodies, acting as protective colloids, which permits the precipitation of various kinds of progressively changing materials. Thus, the key to the present problem is that these protective colloids can be removed, not only by physical solution, but by chemical oxidation. This theory, based so closely on ascertained chemical analyses, receives support by the reverse process—the synthesis of bitumen of correct properties and composition by the production within it of colloidal carbon in asphaltic oil distillates by means of the electric discharge between carbon poles.

This paper has been somewhat vigorously controverted by Hackford on the basis of disagreements on the identity of the substances referred to, and on the chemical changes involved.[196] The problem is obviously not solved yet.

It is remarkable that practically no work has been done on the formation of rock asphalt of the type that is found at, say, Val de Travers. It is commonly assumed that natural bitumen has penetrated porous limestone or sandstone rock, and there the subject has been left, in spite of the fact that a similar impregnation carried out to-day does not yield a product comparable to the natural substance. It has, however, been suggested[73] that the sulphur, which was present in the original decomposing organic matter, sulphonated the fatty acids which resulted from the splitting of the fats. This thionised fatty acid then united with the limestone to form an alkali salt of the acid.

In spite of the fact that experiments in the laboratory have produced a material closely resembling the natural rock asphalt, it is difficult to see how most of the bitumen can be removed from such a chemical combination by simple extraction with solvents. (See also [74].)

CONNECTION OF BITUMINOUS SUBSTANCES WITH COAL AND WITH ONE ANOTHER.

An outstanding feature of much interest in this study is the weight of evidence showing a close connection between bitumen and coal, not merely as parallel products, but in the actual chemical relations that connect them by definite chemical changes. All the links of the complete chain have not yet been forged, but that there is a relationship cannot be doubted.

The earliest, and indeed the only, suggestion of this kind within the period under survey considers coal to be of inorganic origin,[61] the flora being incidental and merely useful in determining the period of formation. The difference between coal and bituminous substances is only a matter of hydrogenation, the former losing hydrogen at high temperatures, through, most probably, the agency of sulphur.

It has been found that asphaltenes (the portion of bitumen insoluble in light naphtha) and other similar conversion products of petroleum react towards chemical reagents in a manner very similar to that of coal. They are compounds also of high molecular weight, but containing more carbon and hydrogen than coal, and less nitrogen and sulphur.

Asphaltenes and coal both swell greatly on heating, but, unlike coal, the former are soluble in carbon disulphide, benzene, and carbon tetrachloride, and are dark brown to brown-black and matte or slightly bright.

Carbenes, which occur in some asphaltites such as grahamite, and are insoluble in carbon tetrachloride, are quite like coal in colour and surface, but unlike it in being soluble in carbon disulphide.

More profound changes in oil products lead to the formation of carboids such as are contained in albertite (a "kerite"), which are of deep black colour, shining surface, and resemble coal in being insoluble in organic liquids.

For the experimental comparisons that are made, the following substances were used:

Asphaltenes, 33 per cent. yield from hard Galician petroleum pitch.
Carbenes, 80 per cent. yield from West Indian grahamite.
Carboids, 88 per cent. yield from Nova Scotian albertite.
Coal (bituminous), C 80 per cent., H 4·9 per cent., S 1·5 per cent., N 1·3 per cent., O 4·9 per cent., Ash 5·5 per cent., coke 80 per cent.

All three petroleum derivatives show very characteristic behaviour with sulphuric acid in forming water-insoluble addition products; coal acts similarly.[29] On addition of acid there is spontaneous heating. After several hours' standing (overnight), water is added, and the liquid is filtered and washed cold. The grey-black mass is decomposed by boiling with water or dilute hydrochloric acid; but it is stable to alcoholic potash. If drying at a high temperature is avoided, the sulphuric acid compound is soluble in pyridine, and water can be added without causing opalescence. The dilute solution is precipitated by mineral acids, and by calcium chloride, ferrous sulphate, silver nitrate, etc., forming metallic salts.

If the action of sulphuric acid in the cold be followed by two hours' warming on a water bath, the yield rises and the sulphur content increases. All reaction products are now insoluble in pyridine. With fuming sulphuric acid the yield rises still higher, but the reaction with water and dilute hydrochloric acid remains the same as before. But warming with concentrated aqueous potassium hydroxide now causes the carboid and the coal compounds to give up a considerable proportion of their sulphuric acid, and the sulphur content becomes the same as that in the products of action of strong sulphuric warmed. The reaction product of asphaltenes and carboids with fuming acid are stable towards aqueous potassium hydroxide.

Concentrated sulphuric acid, when added to finely powdered bituminous compounds or coal floating on methylal, gives formolite. Chlorsulphonic acid acts energetically in the cold, but the reaction products contain no notable amount of chlorine.

The action of nitric acid is also characteristic. The dark brown dinitro-compounds that are formed are completely soluble in acetone, except nitro-coal, which leaves a small residue, even if it is treated at once, whilst still moist, with acetone. The residue on further treatment gives more acetone-soluble material, of a shining, not sooty, appearance. All nitro-compounds are very slightly soluble in ether, light naphtha, benzene, alcohol, acetic acid and chloroform; easily soluble in acetone, dichlorhydrin and pyridine. Concentrated sulphuric acid dissolves them easily in the cold, and pouring the liquid into water causes the precipitation of black, insoluble acid compounds. The acetone solution of nitro-bodies may be precipitated by an ether solution of ferric chloride or mercuric chloride, as double compounds.

Nitro-compounds and N/2 alcoholic potassium hydroxide, when mixed, cause spontaneous heating, but no solution. On removal of alkali, the residue completely dissolves in water to deep brown (colloid ?) solution and froths like soap, but less so. Precipitated by silver nitrate, calcium chloride and ferrous sulphate, there are formed the corresponding salts. Mineral acids produce a brown-black precipitate, which is easily soluble in alcohol and acetone, but insoluble in light naphtha, benzene, ether, chloroform, glacial acetic acid and acetic anhydride. Pyridine acts on nitro-compounds like alcoholic potassium hydroxide; the solution is miscible in all proportions with water, and is precipitated by mineral salts and acids. In the filtrate is found nitrous oxide, present also when potassium hydroxide is used; ammonia results when potassium hydroxide replaces pyridine with no formation of nitric and nitrous acids. Pyridine, alkalis and alkaline carbonates apparently cause isomerism, the nitro-bodies changing to alkali salts of isonitro-compounds. Acidification causes partial decomposition of the iso-body, together with intramolecular oxidation, which results in the production of nitrous oxide. These facts are summarised in Table II, which includes numerical results of the reactions just described.

TABLE II.

Action of Sulphuric Acid and Nitric Acid on Bituminous Substances and Coal.

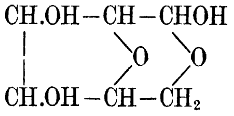
	Concentrated H_2SO_4 at Room Temperature.		*Concentrated H_2SO_4 at 100° C.*		*Fuming H_2SO_4 at 100° C.*	
Material.	S *Content per Cent.*	*Yield per Cent.*	S *Content per Cent.*	*Yield per Cent.*	S *Content per Cent.*	*Yield per Cent.*
Asphaltenes	0·16	110	4 7	115	6·4	138
Carbenes ..	2·60	106	6·2	110	7·8	156
Carboids ..	0·24	100	2·5	119	5·5	119
Coal ..	1·50	110	5·1	115	5·5	134

	Fuming H_2SO_4 at 100° C.		*Action of Fuming Nitric Acid.*		
Material.	S *Content per Cent.*	S *Content after Action of Alkalis per Cent.*	*Yield per Cent.*	*Acetone Soluble Portion per Cent.*	N *Content of Soluble Portion per Cent.*
Asphaltenes	7·6	7·3	127	Completely soluble	6·2
Carbenes ..	10·1	10·1	124		50·0
Carboids ..	6·8	5·4	121		5·3
Coal ..	7·9	5·5	130	111	4·8

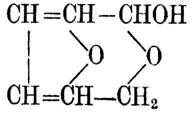
The behaviour of coal towards nitric acid shows no free carbon, but more likely cyclic compounds, to be present in the coal. Oxygen is not present as carboxyl, nor as phenolic hydroxyl, as the coal is only very slightly saponifiable. The majority cannot be present as alcoholic oxygen, as sulphuric and nitric acids would then give saponifiable esters; and also, sulphur chloride (S_2Cl_2) has no action. Aldehydes cannot be present, as they are too easily changed. The oxygen is not ketonic, as coal and asphaltenes are very similar, and the mode of formation of the latter is not such as to produce ketones. It can, therefore, only be present in chain formation, where it behaves as oxonium oxygen.

These oxygen compounds are probably closely connected with the cellulose of the original vegetable growth, as early decomposition products.

Green's formula for cellulose is:



which could lose water and be converted to a furane compound;



which would polymerise—*i.e.*, resinify. If such a compound existed in coal, cumarone and phenols would appear on distillation, and this is what occurs.

The carboids from fatty waxes and resins give no such compounds. It is the mixture of carboids with such resinified furane derivatives and other compounds of cellulose decomposition that gives rise to the different kinds of coal. The similarity between the behaviour of carboids and coals towards sulphuric acid, etc., is due to the cellulose products of coal being oxygen ring compounds and constituents of carboids having also polycyclic oxygen ring structure, though not of cellulose origin.

Sulphur is mainly combined with the mineral matter.

In organic compounds it is in chain formation like the oxygen.

Nitrogen compounds consist of hydrogenated pyridine bases and quinoline compounds probably the same as in coal.

A further connection between these substances and coal is the parallel between asphaltogenic acids and humic acid,[34] which is the mother-substance of coal.

The constitution is not worked out, but it doubtless contains a furane nucleus, because furane and the furfurol occur among the products of distillation; and also because humic acid can be made from furfurol by heating it with concentrated hydrochloric acid followed by fusion with potassium hydroxide or heating with soda and lime. Humic acid reacts with sulphuric acid and with nitric acid like the asphaltenes and asphaltogenic acid.

Humic acid in peat is doubtless a primary product of cellulose. In lignite there is much less humic acid, but what there is resembles in composition that of peat. There is still less humic acid in coal and none in anthracite. Analogously, there is less asphaltogenic acid in the asphaltites formed at higher temperatures than in the others.

Cellulose also gives rise to humins (anhydrides of humic acid) and to petroleum resins. Humins are found with humic acid and cellulose esters in peat and lignite. Petroleum resins, with asphaltogenic acids, are formed when mineral oils are heated a long time in air. They are present in considerable quantities in natural materials, but less so than asphaltenes; carbenes and carboids are found in asphaltites. The comparison between the two series of compounds is very close: Peat—lignite — coal — anthracite. Petroleum resin — asphaltenes — carbenes—carboids. (For further information on humic acids, see [67].)

These theories and facts have received further substantiation[23] by the very close similarity between the substances separated by selective action of various solvents from the pyridine extract of coal, from albertite and from artificially oxidised transformer and lubricating oils. Together with this is the conversion by gentle heat of a bitumen-like substance found in coal into an insoluble material as in albertite; and the fact that artificially produced kerites from oil yield products, on distillation, exactly like those obtained from the "kerites" of coal.

Having traced the interconnection between the constituent classes of compounds of bitumen and its associates with one another and with coal, it remains to indicate the similar relationship between the various bituminous substances themselves.

It has been seen that progressive action of oxygen and sulphur causes increasing molecular complexity and increasing solubility of the products, accompanied by a slow diminution of the proportion of oxygen and the conversion of asphaltogenic acids to anhydrides; so that the metamorphic course of events must be:

Petroleum ——> naphthenic acids ——> asphaltogenic acids ——> asphaltenes ——> carbenes ——> carboids; giving rise to: petroleum ——> bitumen ——> asphaltites (gilsonite, grahamite) ——> "kerites" (albertite, wurtzilite).[68, 69]

The course of these changes is supported by the observation that bitumen is a surface material, whilst the others occur as subterraneous veins, a position where heat and pressure would assist chemical change.[70]

Further support is found in the nature of the products of distillation *in vacuo*.[71]

Deerfield bituminous coal yields mostly C_nH_{2n-4}, also C_nH_{2n}; no C_nH_{2n-2}.

Malone petroleum (neighbouring) yields C_nH_{2n-4}, also C_nH_{2n-2}. C_nH_{2n} would probably be discoverable if larger quantities had been distilled.

Gilsonite gives C_nH_{2n} and C_nH_{2n-2}, resembling petroleum, and containing more nitrogen than petroleum.

Grahamite resembles gilsonite.

The above results may be taken as showing (*a*) coal to be intermediate between vegetable matter and petroleum; (*b*) that gilsonite and grahamite are of organic origin. This is further supported by cholesterol being found in Italian bitumen.[31]

CHAPTER III

PHYSICAL AND CHEMICAL PROPERTIES

BITUMINOUS substances are a nightmare to the investigator, and therefore a fascination. The constituent substances are of such high molecular weight that within the limits of each family, each has little difference from its fellows in any property other than its melting-point. The composition is never quite constant, and may vary considerably, so that there is no definite standard for reference. The only positive scientific property—"scientific" in contradistinction to the semi-arbitrary nature of the mechanical and physical tests—is that based on selective solution, which, at best, is only a method for separating groups of compounds.

All the rest are negative. It is not a liquid, and it is not a solid, according to the ordinary mechanical interpretation of these terms. It cannot be examined without some preliminary treatment; as it is not always homogeneous, even mild heating disturbs it considerably. It has no definite melting-point. No optical test can be applied; without fear of serious change caused by dilution, it is not possible to witness precipitations in the ordinary way; only one ordinary electrical test can be applied; when any operation is carried out on it, it cannot be recovered in an unchanged condition; it does not remain constant even when left alone.

Therefore, the number of tests that are applicable are limited, and it is seldom that a series of experiments exactly confirm one another; so that when a particular point is being investigated a number of tests of other properties should be made to ascertain how far, as a whole, the material is not remaining constant in its general condition.

The cause of change due to chemical activities has already been discussed, but the cause of physical change resulting from simple heating and cooling is worth examining.

Bituminous substances consist of several groups of compounds—saturated, unsaturated, paraffinic, naphthenic hydrocarbons, sulphur and oxygen derivatives, some perhaps in colloidal form, and some mineral matter, free, or combined in the form of metallic salts.

It is justifiable to suspect, indeed, to consider as certain, that, when such a mixture is heated and cooled, the order of separation of the constituents will vary with the velocity of cooling; and that if the substances present are different in their nature they may exert a very definite influence on the extent of one another's change from the liquid to the solid state, and the degree of dispersion of the colloidal matter. Thus the simple operation of heating and cooling may give rise to a considerably changed physical condition; and profound changes may result from the equally simple operation of solution and recovery.

The fewer the substances present the more sharply defined will be the properties of the mixture, and this has been observed characteristically in the comparison of samples of bitumen containing a greater or less proportion of paraffin wax in the artificial, and ceresine in the natural, products.

The presence of paraffin is bound up with the appearance of the bitumen, causing it to appear dull and greasy of surface, and such material shows great changes when dissolved and recovered.

A full account of the properties of bituminous substances will, however, not be given here, as these have, in the main, been realised and established long ago. Nor will there be repeated the detailed descriptions of the various tests as are found in well-known textbooks on the subject. Concerning two properties, however, attention is especially alive and investigation is proceeding, and among the tests there is much that is of interest to be set down concerning their development and significance.

PHYSICAL PROPERTIES.

Light-Sensitiveness.—The remarkable recrudescence of interest in the changes that light produces in bitumen inevitably raises enquiry as to how it originally began. Joseph Nicéphore Niepce (1765–1833), having interested himself in the practice of lithography, pondered on the problem of reproducing the colour of a picture. By good luck he had at hand a lens suitable for use in a camera, and obtained results in May, 1816, though not in colour, by a method undescribed. After making further experiments he employed a solution of "asphalt" dissolved in Dippel's animal (bone) oil, a liquid already known to be sensitive to light; but what led him to try bitumen is impossible to tell. By this means he produced, in 1824, a portrait on tin of Cardinal Georges d'Amboise, which, though requiring subsequent strengthening by engraving, was undoubtedly the first "heliograph" in the world.[75] In earlier experiments he used lavender oil as a solvent, and fixed the plate by removal of the still soluble material with a mixture of lavender oil and petroleum, followed by a final washing with warm water.[76]

Judean bitumen was to be preferred in such a process, and investigators began busily to seek the specially active component present in the complex mixture, and ways to increase the sensitiveness of the material. It was found that the different portions possessed a light-sensitiveness quantitatively different but qualitatively the same, the more condensed being acted on to a greater degree than the less.[31] This was subsequently substantiated if the "condensation" is measured by the proportion of sulphur in the materials, the element which, with oxygen, causes this change most actively.

It was found that the alcohol-soluble (α) resin was of no value; that the ether-soluble (β) resin was of only partial usefulness; but that the ether-insoluble chloroform-soluble (γ) resin showed the greatest effect. Therefore, improvement in the sensitiveness of the bitumen could be attained by treatment with ether in order to remove the actinically inert material. Valenta found, however, that the inactive substance could be converted into the active by fusion with sulphur (which leads to partial coking); by heating with 12 per cent. flowers of sulphur, with pseudo-cumene (b.p. 170°) as solvent under a reflex condenser and subsequent extraction with benzene; or by the action of 6 to 8 grs. sulphur chloride to 100 grs. of bitumen in solution in five to six times the quantity of carbon disulphide.

$$1.\ 2\,\underset{\alpha\text{-Resin}}{C_{32}H_{46}S} + 2S = \underset{\beta\text{-Resin}}{C_{64}H_{92}S_3}.$$

$$2.\ \underset{\beta\text{-Resin}}{C_{64}H_{92}S_3} + 5S = \underset{\gamma\text{-Resin}}{2C_{32}H_{42}S_2} + 4H_2S.$$

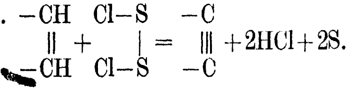
The action of sulphur chloride is a general one, and produces substitution and addition products with, naturally, elimination of hydrochloric acid.

The quantitative effect of thionisation is, in general, not to be foreseen, and whilst a Cuban bitumen is as good as the Judean, the sensitiveness attained in them all is not proportional to the percentage of sulphur.

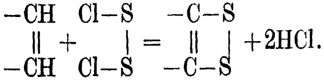
The insolubility of the bitumen in solvents after exposure to light has been ascribed to the catalytic effect of minute traces of oxygen, a suggestion which calls for the attention of the quantum theorists, as bitumen is sensitive to the whole range of the visible spectrum wit a portion of the ultra-violet as well.[77, 78]

This action of sulphur chloride has been employed fro time to time as a general thionising agent. To conve the resins, solid, orange-red or orange-yellow residu of the distillation of crude petroleum, into useful bituminous substances[79] resembling Judean bitumen—th author of the process took this material as a standar probably without knowing how it fitted into the genera scheme of development of the subject—they are melte and treated with 1 to 5 per cent. or more S_2Cl_2 (dissolved in 10 to 20 per cent. of its weight of CS_2), accordin to the hardness required. The disengagement of aci vapours indicates the length of time of heating; an when the mass cools it is found to have a melting-poin 20 to 40° C. above that of the material employed. I was found that treatment by chlorine or sulphur, dissolved in carbon disulphide, did not give as promp and economical results.

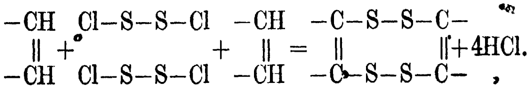
This reaction has been studied[80] quantitatively (wit continuous passage of dry air through the mixture) with the careful exclusion of the presence of moisture. Under these conditions of reaction only hydrochloric acid is evolved; no sulphuretted hydrogen could be detected. The interim suggestions as to the course o action are three :

1.


$$\begin{array}{l}-\text{CH}\\ \quad\|\\ -\text{CH}\end{array} + \begin{array}{l}\text{Cl}-\text{S}\\ \qquad|\\ \text{Cl}-\text{S}\end{array} = \begin{array}{l}-\text{C}\\ \quad|||\\ -\text{C}\end{array} + 2\text{HCl} + 2\text{S}.$$

2.


$$\begin{array}{l}-\text{CH}\\ \quad\|\\ -\text{CH}\end{array} + \begin{array}{l}\text{Cl}-\text{S}\\ \qquad|\\ \text{Cl}-\text{S}\end{array} = \begin{array}{l}-\text{C}-\text{S}\\ \quad\|\quad|\\ -\text{C}-\text{S}\end{array} + 2\text{HCl}.$$

3.


$$\begin{array}{l}-\text{CH}\\ \quad\|\\ -\text{CH}\end{array} + \begin{array}{l}\text{Cl}-\text{S}-\text{S}-\text{Cl}\\ \\ \text{Cl}-\text{S}-\text{S}-\text{Cl}\end{array} + \begin{array}{l}-\text{CH}\\ \quad\|\\ -\text{CH}\end{array} = \begin{array}{l}-\text{C}-\text{S}-\text{S}-\text{C}-\\ \quad\|\qquad\qquad\|\\ -\text{C}-\text{S}-\text{S}-\text{C}-\end{array} + 4\text{HCl}.$$

Colloidal Phenomena.—An important step forward in the understanding of the mechanism of light-sensitiveness was the recognition of its close connection with colloidal phenomena, which appears to dispose of the suggestion of catalytic oxidation. The behaviour of the material during the driving off of the solvent is that of a colloid, and the addition of sensitisers not only causes increased sensitiveness to light, but also to heat, and causes insoluble material to become soluble in chloroform.[81]

More direct evidence shows[82] raw Judean bitumen to be a mixture in molecular and colloidal dispersion, and the sensitive γ-resins to be in a colloidal state. The deduction that ultra-filtration would increase the sensitiveness is supported by experiment; light, therefore, acts by its coagulating effect, and not by stimulating oxidation.

That bitumen does exist as a colloidal suspension has been revealed by the ultra-microscope. Precipitation can be brought about by the addition of light petroleum naphtha and also by electrolytes,[83] such as through chloride, bromine and gaseous hydrochloric acid, dissolved in mineral oils, particularly in benzine. These experiments do not command trust, as the electrolytes were dissolved in the very substance that, by itself, causes precipitation. The results are stated to be good, although quantitatively dependent on conditions, and affected to an unknown degree by the formation of addition compounds.

These observations are of interest, as there is obvious connection between them and the Willite patents, which cover the addition of sulphates, particularly copper sulphate, in order to increase the tensile strength of the material.[84, 184, 185] Suggestive, too, is the use of anhydrous alum or the like, primarily for the purpose of dehydration at a temperature below that necessary to drive off the water by heat.[192]

Obviously, there is necessary a considerable amount of research before the matter is satisfactorily settled, and here is work both of theoretical and practical value; for example, it is unknown how far light contributes to the ageing of asphalt pavements—how far the "pathological" crumbling away of the surface or weakening of tenacity depends on the "de-colloidification" of the bitumen by light. Such action is by no means impossible, as further investigation on the hardening of bituminous substances, which has been found to be qualitatively independent of loss of lighter substances by volatilisation, has led ultimately to the opinion that the increase of insoluble matter is possibly due to the action of light and heat rather than to oxidation.[85, 86]

We have just been considering a certain property of a colloidal constituent of bitumen, and now quite another section of colloidal science will be reviewed, where bitumen as a whole acts as a dispersoid for finely divided adventitious mineral matter. The subject has been touched on in the reference to the formation of Trinidad asphalt and may usefully be extended, as it is of high importance to most of those industries in which bitumen is employed.

In road mixtures and mastic the presence of finely divided "filler" is essential, in order to convert the very viscous liquid bitumen to a relatively immovable mass. Sand has its definite uses, but is a coarse material, and its separation from any mixture is a simple matter. A very fine material such as clay has peculiar properties, and it is the absorption by the clay of bitumen and the capacity of the bitumen to keep the clay in suspension that constitutes an interplay of properties and forces that have such valuable industrial results.

Trinidad asphalt has been studied to the greatest extent, partly because of its long-standing industrial use, partly on account of the interesting phenomena it presents, and partly because of the very unusual geological occurrences that have caused its production.

It will be remembered that the analysis of Trinidad asphalt is:

	Per Cent.
Water and gas, loss on drying at 100° C. ..	29·0
Bitumen, soluble in cold CS_2	39·0
Mineral residues, after ignition	25·2
Organic matter, not bitumen, by difference ..	6·8
	100·0

The water is in a most peculiar condition, in that there is no immediate indication of its presence. This is an example of the property of finely divided material to take up a liquid and yet appear to be dry, a surface action which, in such a case of water and clay, may be associated in part with incipient hydrolysis of the silicate. It is tempting to suggest that it is this mixture of two liquids and a fine solid that makes for the mechanical stability of the whole material, but in the light of what comes just below this is scarcely tenable. But it is the fact[87] that a mixture of bitumen and dry clay is not so firm in consistency as a mixture of the bitumen and the clay in form of a slurry.

If Trinidad asphalt, or even an artificial mixture of clay and water with bitumen, be dissolved out in carbon disulphide, no water separates. On the other hand, such a separation can be caused by alcohol. Notwithstanding these observations, there is undoubtedly some equilibrium between clay-and-water, which will mix with bitumen, rather than clay-and-bitumen, which will not mix with water, an observation throwing much confirmatory light on the theory for the formation of the

Trinidad asphalt lake. And further, it has been observed that such an artificial mixture rapidly loses water till this has fallen to 29·5 per cent., the quantity (together with gas) that is present in the lake product itself.

The above statement about the clay-water-bitumen equilibrium must be modified in one particular—that emulsification, with water as the "external" phase, is made possible by the addition of a hydrocarbon flux.[88]

Other colloidal properties that are exhibited are those of suspension and Brownian movement, or pedesis. A very dilute "solution" of Trinidad asphalt in carbon disulphide showed after one month a content in mineral matter of 4·5 per cent.; after three months, 2·57 per cent.; with substantially no change after six months,[62] indicating a stability of composition that is the more remarkable considering the material has been interfered with by such dilution (see also [89]). An examination of this solution by the ultra-microscope, a method of investigation which appears to have been first applied by Holde,[90] showed the mineral particles to be in a characteristic condition of active movement.[62] If some Trinidad material be dissolved as a 10 per cent. solution in benzol, centrifugated for half an hour, allowed to stand for a month, and passed through a Chamberland ultra-filter, there are still some particles to be found.[87]

Such intimate relations between bitumen and finely divided mineral matter are well known in the petroleum refinery, where filtration through particularly chosen clays and the like is a valuable method of purification. This phenomenon has been studied also by the analyst to find how far such absorbed bitumen can be extracted quantitatively from its mixtures. Known mixtures were made up with a pure gilsonite and a variety of finely divided fillers, when it was found that the bitumen dissolved out, together with the quantity of mineral matter obtained on ignition, left a difference, unaccounted for, of anything up to about 9 per cent.

TABLE III.

QUANTITATIVE EXTRACTIONS OF BITUMEN

	Extraction by Ordinary Methods (Per Cent.).	*After Maximum Extraction (Another Series of Experiments) (Per Cent.).*
Fuller's earth, air dried	8·9	—
„ „ ignited	6·2	5·80
„ „ Florida	—	8·94
Brick clay, air dried	4·8	—
„ „ ignited	4·2	—
„ „ New Jersey, air dried	—	1·24, 1·28
„ „ New Jersey, dried 120°	—	1·07, 1·28
Portland cement, ignited ..	1·6	—
Trinidad mineral residue,* ignited	1·3	8·90
White clay (Massachusetts) ..	—	1·28, 1·03

Filtration experiments with a mixture of a 0·1 per cent. solution of the same gilsonite in carbon disulphide and mineral matter ground till 90 per cent. passed a 200-mesh sieve showed that the action of fuller's earth is selective: a softer, malthene, hydrocarbon was retained, which was subsequently incompletely dissolved out; powdered limestone behaved less effectively, and ground silica and Portland cement showed no absorptive capacity —a contradiction (in the latter case) with the figure in the above table. Experiments with Trinidad bitumen show the same general results, but less developed, a difference which has been ascribed to the lower molecular weight of this material.[91]

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* Doubtless profoundly modified by separation and ignition (Author).

It has been maintained,[92] in the face of contradiction, that the resins are more adsorbed than are the paraffins; and that, among the latter, those of higher molecular weight are adsorbed to a greater degree than those of less complexity.

Very significantly it has been shown that such adsorbed material has, to a considerable degree, similarity to kerogen in oil shale.[197, 198]

A somewhat different deduction must be made when certain metallic salts, such as lead acetate, ferrous sulphate, zinc sulphate, and particularly copper carbonate or basic carbonate are mixed with bitumen. Reduction of the basic carbonate, for instance, to cuprous oxide takes place, and an enormous degree of dispersion occurs; with the more stable copper sulphate this is considerably less. The supporting value of the bitumen is directly proportional to the number of particles, and so is a measure of the ease with which chemical action takes place.[95]

With a material so discouraging in appearance as bitumen, it is not surprising that very little work has been done on its optical activity; but one isolated investigation deserves notice.[96] The portion that is soluble in petroleum ether of Val de Travers asphalt, Syrian bitumen, Alsace crude oil and a fraction from Welser bitumen has been examined in the following fashion. The solution was evaporated, taken up in chloroform, and acted on with ozone. It was then treated with anhydrous tin chloride, followed by sodium hydroxide, and finally diluted with petroleum ether and filtered. The resulting oil was denser than water and always contained resins. The optical activity, which could be increased by repeated ozonising, was found to belong to one of the less reactive of the saturated substances present. The figures obtained were, for example:

Syrian bitumen, $a_{30}=+1{\cdot}4°$. Val de Travers bitumen, $a_{30}=+3{\cdot}4°$.

Surface Tension.—This rather elusive property is of enormous importance, as on it depends the stability of asphalt roads and mastic mixtures. It has not been as much investigated as it deserves, and such a simple and important technical question, for instance, as to why bitumen will adhere to sand and not to flint is still unanswered. Such results as have been obtained have an industrial or analytical value, in which the asphaltic mixture is heated with a solution of salt,[97] in order to separate the bitumen and mineral matter by means of their different gravities. After they have separated, the one rises and the other falls; but it is a question of surface tension whether they separate at all. Sodium carbonate solution, recommended for a sand-coal tar mixture[98] will not work with Mexican bitumen; whilst a solution of the same substance of a strength of 1 to 1,000 will cause the required change to occur in Canadian "tar sands."[99] In the latter case, indeed in all cases, the required condition is that the surface tension of rock to oil (and the like) must be greater than the surface tension of rock to aqueous solution plus that of oil to aqueous solution.

CHEMICAL PROPERTIES.

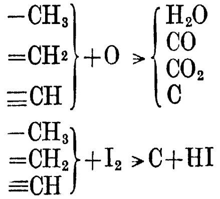
The quantity of detailed chemical facts that are known about bitumen and its congeners is not great, and there is, complementarily, a large amount of investigation still to be done. The subject is one of very considerable difficulty on account of the general nature of the material which has already been outlined.

The chemical treatment of the problem has already been described (see p. 12), and the separation by selective solvents is well established. There are, however, some investigations that have been carried out during the period with which we are concerned that are such as to demand attention.

Action of Halogens.—This, at first sight only, is remarkably different in the cases investigated.

The passage of *chlorine* into a bitumen of the consistency of soft pitch at 200° C. converts the material into a brilliant mass with a crystalline fracture, melting above 150° C.[100] (See also *G.P.*, 228, 497, 1909.)

Iodine, contrary to the usual statements, reacts with hydrocarbons, producing hydriodic acid and carbon. It is a time reaction, which takes place with even small quantities of iodine without intervention of catalysers. The action is one of reduction without substitution, and is to be compared with the effects of oxidation:



$$\left.\begin{matrix}-\mathrm{CH_3}\\=\mathrm{CH_2}\\\equiv\mathrm{CH}\end{matrix}\right\}+\mathrm{O} > \left\{\begin{matrix}\mathrm{H_2O}\\\mathrm{CO}\\\mathrm{CO_2}\\\mathrm{C}\end{matrix}\right.$$

$$\left.\begin{matrix}-\mathrm{CH_3}\\=\mathrm{CH_2}\\\equiv\mathrm{CH}\end{matrix}\right\}+\mathrm{I_2} > \mathrm{C}+\mathrm{HI}$$

there being much more carbon resulting from the latter reaction than from the former.[101]

The differences in the reactions between chlorine and iodine are superficially different, but in the light of Nellensteyn's work on the oxidation of asphaltic oils the phenomena may be the same. Iodine is considered to act like oxygen and to destroy the protective colloids that keep colloidal carbon in suspension; a result which seems to be, in general, similar to that of the action of chlorine, so our well-established custom of looking on the halogens as a closely related family is not disturbed.

Analysis.—A suggestion, more interesting, apparently, than practicable (as it does not seem to have been followed up), is that of analysing a sample by fractional precipitation[102] instead of selective solution. The sample is dissolved in carbon disulphide—a solvent found to be preferable to 90's benzole[103]—and the "asphaltum" (asphaltenes) precipitated by hexane. The hexane-soluble material is then precipitated by methyl alcohol, and the residue obtained by evaporation constitutes the third class of substances to be separated.

Formolite Reaction.[104]—Nastjukoff's reaction gives a measure of the proportion of unsaturated substances present in a mixture, and consists in chemical reaction with formaldehyde and concentrated sulphuric acid.

To avoid carbonisation of the material by the action of the acid and also the subsequent formation of an emulsion, the usual procedure is modified by dissolving the sample in light naphtha and treating it with concentrated sulphuric acid and paraformaldehyde in place of 40 per cent. formol, and extracting the unchanged substances from the precipitate. It was also found that the more "asphaltic" a bitumen is the more residue is left by the action of fuming and of concentrated sulphuric acid.

CHAPTER IV

EFFECT OF HEAT

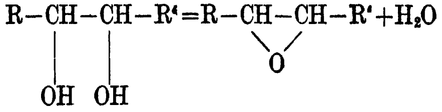
It is universally recognised that bitumen is easily affected, as to its constitution and properties, by the action of heat, but little if any quantitative information is to be found in current literature regarding the nature and extent of the change.

MODERATE HEATING.

Recommendations are continually made against undue heating of the material, but it is not sufficiently emphasised how considerable are the changes of properties that are caused by relatively small degrees of heating, and how long a time is required for the bitumen to settle down again, if it really ever does, to its original condition. A glimpse of this is obtained in the comparison of the ductility and penetration of samples that have been cut cold from bulk with those that have been melted and poured into moulds in the usual way.

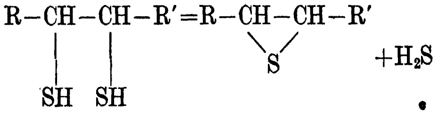
The changes caused by heat are probably three-fold: (1) a physical change, after which the material tends to revert to its original condition, but which it probably never reaches, owing to the temperatures, velocities and conditions of hardening of the numerous constituent substances; (2) a specific chemical change caused by heat; and (3) chemical changes which would take place slowly at ordinary temperatures, but which are accelerated by heat.

Such changes may be exemplified by those found to occur to the asphaltenes.[198] When separated by means of ethyl ether, dried *in vacuo* at 50° C. and distilled, the following reactions occur, in addition to which ammonia (probably from ring-compounds), wax and carbonaceous residue are obtained:



$$R-\underset{OH}{CH}-\underset{OH}{CH}-R' = R-\underbrace{CH-CH}_{O}-R' + H_2O$$

Oxy-asphaltene



$$R-\underset{SH}{CH}-\underset{SH}{CH}-R' = R-\underbrace{CH-CH}_{S}-R' + H_2S$$

Thio-asphaltene Thio-kerole

If, however, the last-named substance is present, no sulphuretted hydrogen is evolved.

Apart from the change of properties the most characteristic result of overheating of bitumen has been claimed to be the formation of *carbenes*.

This group of substances, soluble in carbon disulphide and insoluble in carbon tetrachloride (in which 5 per cent. carbon disulphide makes no difference to the result), was so named by Clifford Richardson. Their presence is considered to be evidence of overheating of the material or of exposure; but general experience seems to show that the practical value of this test, when usually applied, is somewhat over-rated, as they appear only after heating has been very severe, as, for instance, for two hours at 370° C.; when, for comparison, heating for two hours at 230° C. caused the penetration to be roughly halved, with maximum loss of only about 2 per cent. of volatile matter. The existence of carbenes is associated with an increase in fixed carbon and non-bituminous organic matter, so that they are associated with considerable changes in physical properties of the substance, due to molecular re-arrangement. So much so that fixed carbon determinations would probably be useful in tracing such changes due to heat, especially as even moderate heat may so reverse the nature of the material that it becomes more soluble in carbon tetrachloride than in carbon disulphide. Carbenes are probably formed by the cracking of paraffin and asphaltic hydrocarbons, naphthenes and unsaturated substances.[52, 105-108]

A further matter of interest is one that is connected with their estimation. It was noticed that, in certain cases, the quantity of carbenes increased on standing, which suggested that a colloid was being coagulated; also, it was found that light had an important influence in increasing the quantity of carbenes. For this reason two kinds of carbenes were postulated—those precipitated in the dark completely in twelve hours, and those "pseudo-carbenes" completely precipitated in the light in twelve hours. When extraction was carried out in hot weather in the light an odour of hydrochloric acid was noticed, and the precipitated solids contained 3 to 4 per cent. chlorine. It appears, therefore, that light acting on a solution of bitumen in carbon tetrachloride gives rise to a reaction whereby the solvent gives off hydrochloric acid, which then unites with the unsaturated compounds present and precipitates them.[108] (See also [109].)

This occurrence is not isolated; in the case of coal tar and pitch the same is to be observed.[110, 111]

The results of an investigation on the extent of the changes caused by heat are only comparable on the basis of the strictest limitation of the conditions of the experiments; for instance, if experiments are made on the same material, heated to the same temperature for the same time, important differences will result if different quantities are taken for examination—even when care is taken to avoid overheating. The examples of the changes that have been observed are given in Table IV.

TABLE IV.

CHANGES CAUSED IN RESIDUAL BITUMEN BY HEAT.

Residual Bitumen.	*Heated at Degrees C. for 7 Hours.*	*Property.*	
		Before Heating.	*After Heating.*
		Penetration.	
C	177	45	39
	204	45	19
	205	45	26
	(Cut cold, for comparison)	(39)	—
D	204	50	34
		Ductility.	
C	204	98·5	16
	204	+100	11·5
	205	97	15·5
	(Cut cold, for comparison)	(about 20)	—
D	204	+100	+100
		Fusion-Point.	
C	177	55·5° C.	59° C.
	204	55·5° C.	75·5° C.
		Asphaltenes.	
C	177	31·1	34·1
	204	31·1	38·8
		Viscosity.	
C	204	133	181
D	204	261	316

The last two ductility results indicate the important differences that may exist in the nature of bitumens; the latter contained less paraffin wax than the former, and the difference in other behaviour will be met from time to time. These results, together with others, have led to the recognition of regularities sufficiently approximate to be expressed in a mathematical formula, perhaps for the first time.

PENETRATION.

$$Fp = K \times \frac{t \times T \times A}{W},$$

where Fp = fall of penetration.
t = temperature at which the sample was heated, less 25° (the temperature of testing in degrees C.)
T = time of heating, in hours.
A = area of surface during heating, in square cm.
W = weight of sample, in grams.
K = a constant.

Transposing and evaluating for K in order to test how far the relationship really holds, the following figures are obtained:

TABLE V.

PENETRATION CALCULATION.

Bitumen.	K.	*Temperature of Heating in Degrees C.*
C	0·007	177
	0·027	204
	0·035	194
	0·030	204
D	0·017	204
	0·017	204
	0·022	204

A longer series of results are given in Figs. 2 to 9 (see p. 59, *et seq.*).

DUCTILITY.

Employing the above formula, results obtained were—

TABLE VI.

DUCTILITY CALCULATION.

Bitumen.	K.	*Temperature of Heating in Degrees C.*
C	0·039	177
	0·096	204
D	0·120	194

A different series of figures are shown in Figs. 10 and 11 (see pp. 67, 68).

FUSION-POINT.

The same formula, but omitting the time of heating, T, as this was the same in all cases, the figures were—

TABLE VII.

FUSION-POINTS CALCULATION.

Bitumen.	K.	*Temperature of Heating in Degrees C.*
C	0·028	177
	0·160	204
	0·085	204
D	0·091	204

A further series of observations are summarised in Fig. 1 (see p. 58).

LOSS ON HEATING.

The results, similarly treated, gave the following figures.

TABLE VIII.

LOSS ON HEATING CALCULATION.

Bitumen.	K.	*Temperature of Heating in Degrees C.*
C	0·00024	177
	0·00076	204
	0·00067	194
D	0·00061	204

In all these cases the values for K (except the first ones) are sufficiently regular to show that a true law can be traced through the erratic behaviour that the material usually shows. Since the figures showing most deviation are those associated with the more widely differing temperatures, these deviations may be a measure of the irreversible chemical change as compared with the reversible physical change.

A further series of observations have been made with the materials enumerated under "Correlation of Properties" (p. 103), in which this series of single properties have been ascertained and compared to form the subsequent collection of curves.

SINGLE TESTS.

1. *Specific Gravity.*—No deductions can be drawn from these figures.

2. *Fusion-Point* (Fig. 1).—In this graph is more clearly and more accurately demonstrated the increase

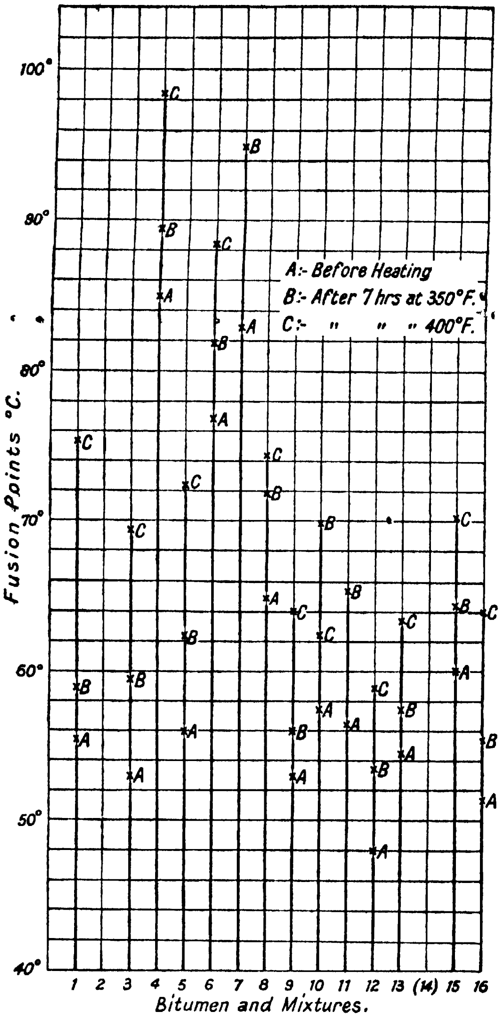


Fig. 1.—Fusion Points.

of fusion-point after heating at successively high temperatures, than would have been the case in the ordinary mode of plotting.

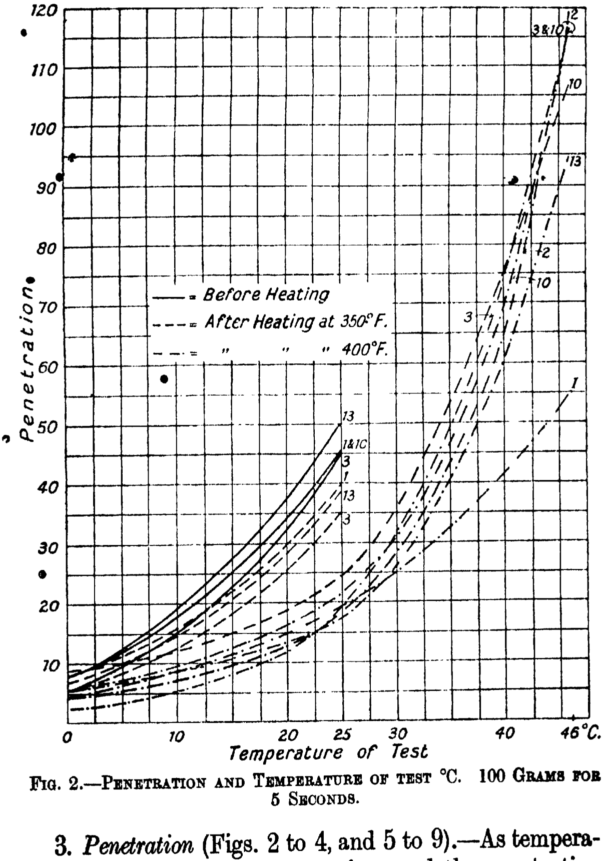


FIG. 2.—PENETRATION AND TEMPERATURE OF TEST °C. 100 GRAMS FOR 5 SECONDS.

3. *Penetration* (Figs. 2 to 4, and 5 to 9).—As temperature rises, the material gets softer, and the penetration figure increases. It is for this reason that Figs. 2 and 4

show curves having no 46° C. point, the materials being too soft at this temperature for a reading to be taken.

Curves obtained from samples heated to 350° and 400° F. conform, as a rule, to the position of a curve

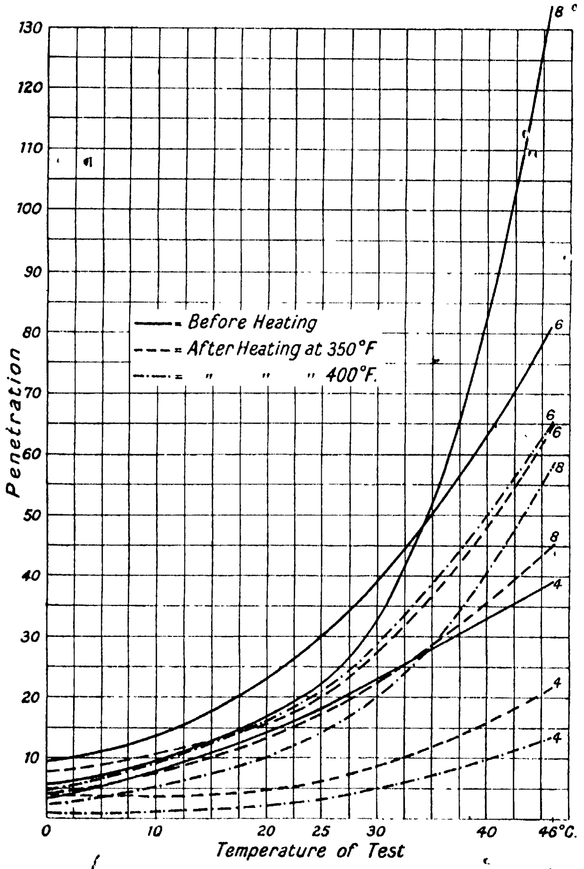


FIG. 3.—PENETRATION AND TEMPERATURE OF TEST °C. 100 GRAMS FOR 5 SECONDS.

being lower the higher the temperature to which it has been heated, indicating, as is to be expected, that the material has become hardened. An exception to this is the uppermost point of 10, which probably indicates

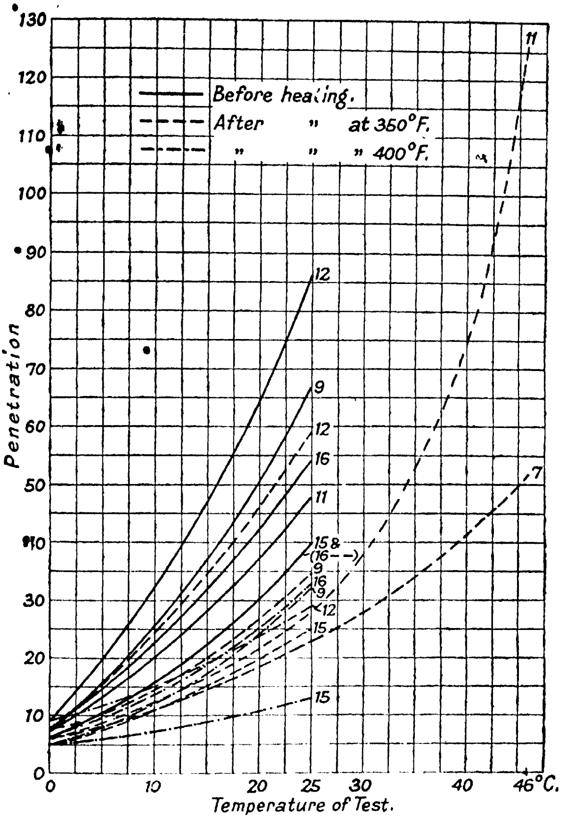


FIG. 4.—PENETRATION AND TEMPERATURE OF TEST, °C. 100 GRAMS FOR 5 SECONDS.

slight decomposition at the respective temperature; but the curve as a whole lies in the position natural to it. The position of the curves for 4 and 6 is normal.

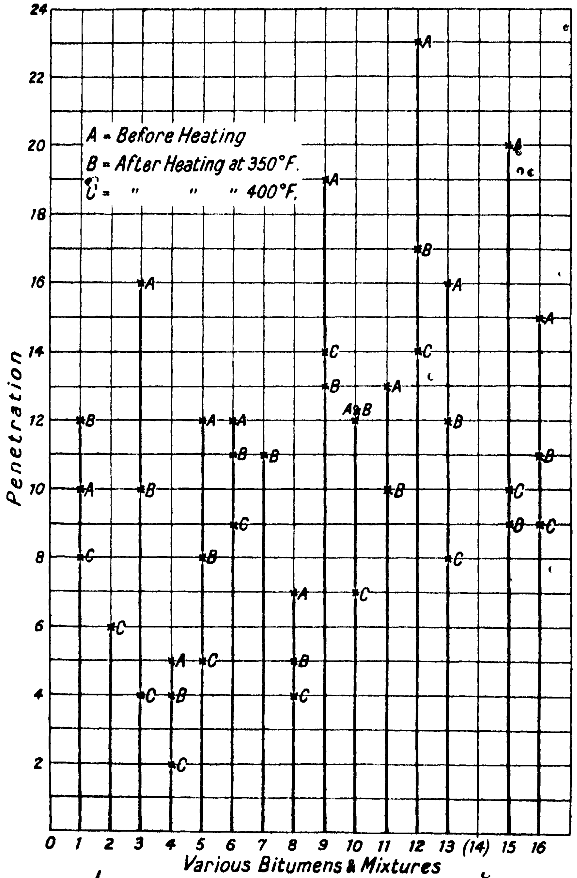


FIG. 5.—PENETRATION TESTS AT 0° C. 100 GRAMS FOR 60 SECONDS.

As 100-gram tests for 5 seconds are the usual tests made, and are therefore the most generally significant, they have been presented in the usual fashion. The remaining tests have been shown in columnar form, because the differences between the figures are mostly so small as to show up badly on a curve, and also because these low results are occasionally anomalous.

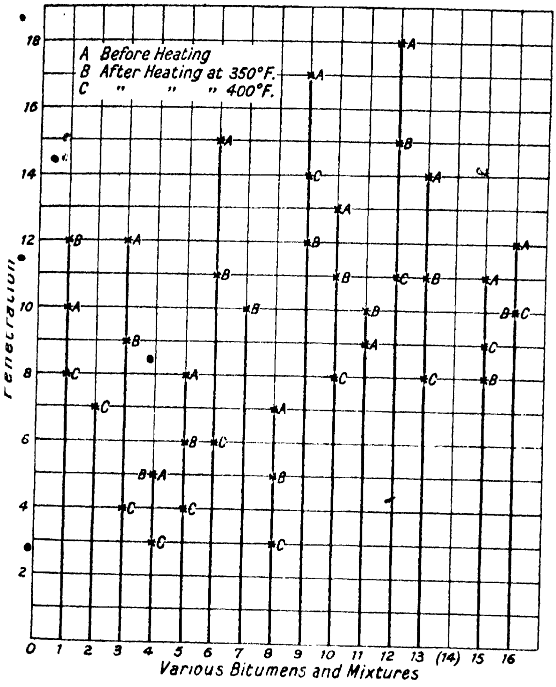


FIG. 6.—PENETRATION TESTS AT 0° C. 200 GRAMS FOR 5 SECONDS.

A further reason for not plotting out the remaining penetration figures is that there is so great a resemblance in shape with the other curves, that only differences of direction or level of lines would be shown without the

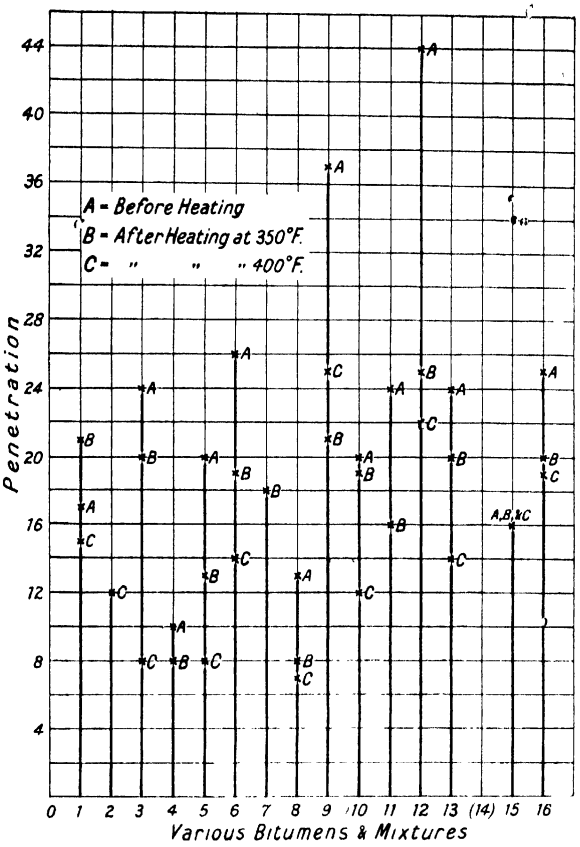


FIG. 7.—PENETRATION TESTS AT 0° C. 200 GRAMS FOR 60 SECONDS.

monstration of anything new. At 0° C. 200 grams for seconds give figures just double those for 100 grams r 5 seconds. The 100 grams for 60 seconds are about vice those for 100 grams for 5 seconds, as are (but with ss regularity) those for 200 grams for 60 seconds.

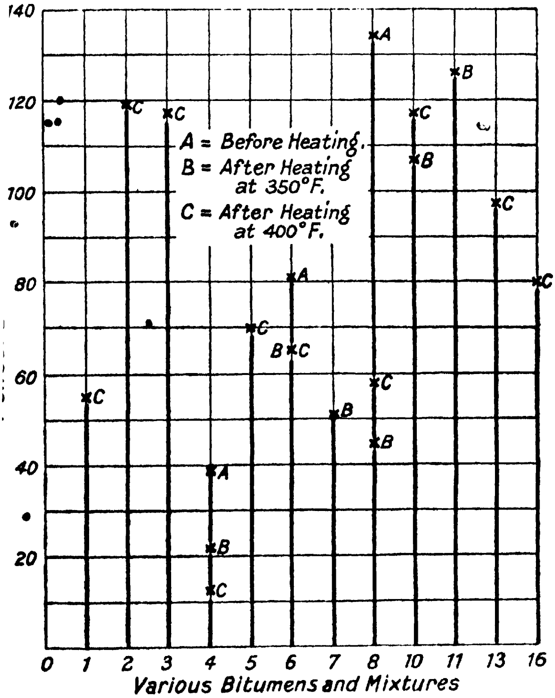


FIG. 8.—PENETRATION TESTS AT 46° C. 100 GRAMS FOR 5 SECONDS.

All the samples of bitumen, individual or mixed, before or after heating at 350° or 400° F., when examined at 0° C. give results lying between 2 and 10, mostly between 4 and 7. Therefore, those materials which show least variation due to the effect of temperature will have the flattest curves, and this indicates the hardest consistency. It is seen, therefore, that, unless an exceptional substance is found, there is no chance

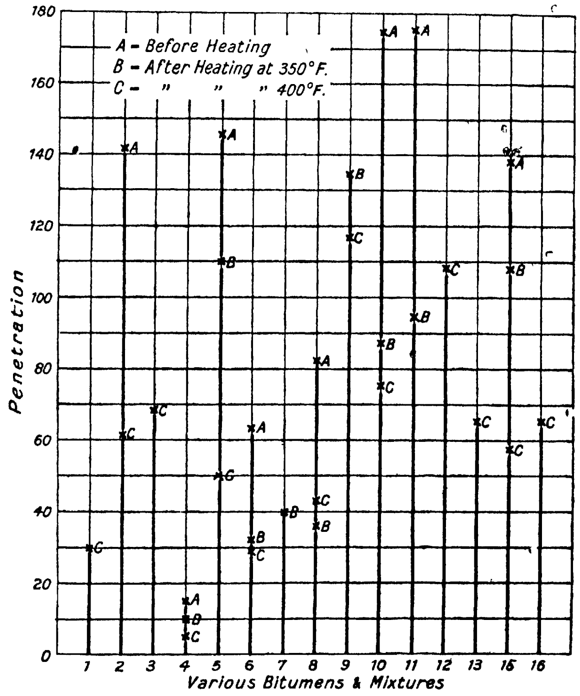


FIG. 9.—PENETRATION TESTS AT 46° C. 50 GRAMS FOR 5 SECONDS.

of obtaining a material of the desired penetration and of low temperature co-efficient.

4. *Ductility* (Figs. 10 and 11).—In these curves no +100-results are included (except three on Fig. 11 for special reasons), as they are necessarily indefinite.

As a result there is a paucity of points for giving direction to some of the curves, but there is very little doubt as to what this actually is.

Interesting curves are those of 9 and 12, Fig. 11. Here evidently the strength of the bitumen has been so weakened by fluxing and elevation of temperature, that the threads are becoming more and more easily broken.

The top point of 8 is indefinite, but has been inserted as giving an indication of the general shape of such a curve, with probably little error with so hard a substance.

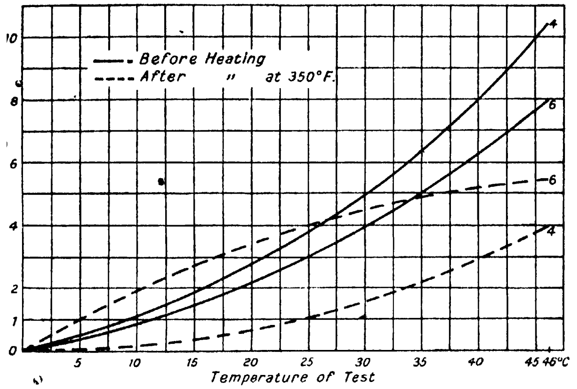


FIG. 10.—DUCTILITY AT VARIOUS TEMPERATURES.

No. 13 shows little difference in ductility before and after heating to 350° F., but falls rapidly in value when heated to 400° F.

No. 16 shows no difference between the figures before and after heating to 350° F., both being +100.

5. *Viscosity* (Fig. 12).—In plotting these curves, only figures obtained for 300°, 350°, and 400° F. have

been included, except in the relatively rare cases when readings at 250° F. are available. Viscosities higher than those over 6,000 were measured by ascertaining the time of formation and fall of one drop; so that they are

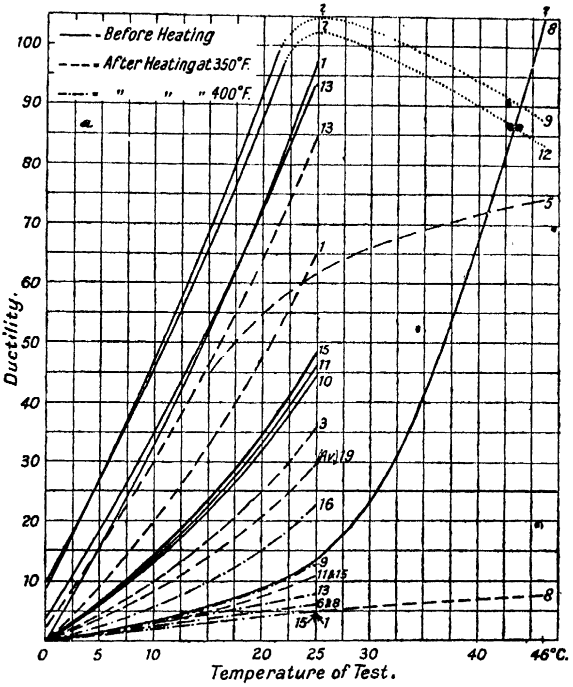


FIG. 11.—DUCTILITY AT VARIOUS TEMPERATURES.

not available for plotting. The approximate position cannot be ascertained by extrapolation, as a great difference is shown by the various materials in their drop-forming capacity, indicating considerable variation surface tension and rate of cooling and solidification t the orifice of the instrument; even, possibly, in the egree of adhesion to the surface of the fine agate exit ube; all these effects would have considerable influence t these very slow rates of movement.

The increase in viscosity of one sample as compared

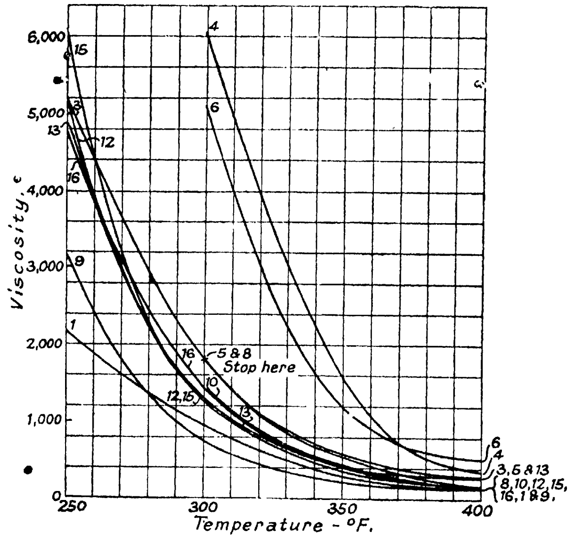


FIG. 12.—VISCOSITY AT VARIOUS TEMPERATURES.

with another may be due either to the increased size of the colloidal suspension[112] or to the increased size of the molecules resulting from polymerisation.

6. *Loss on Heating.*—There is nothing to be deduced from these figures.

7. *Flash-Point.*—There is nothing to be deduced from these figures.

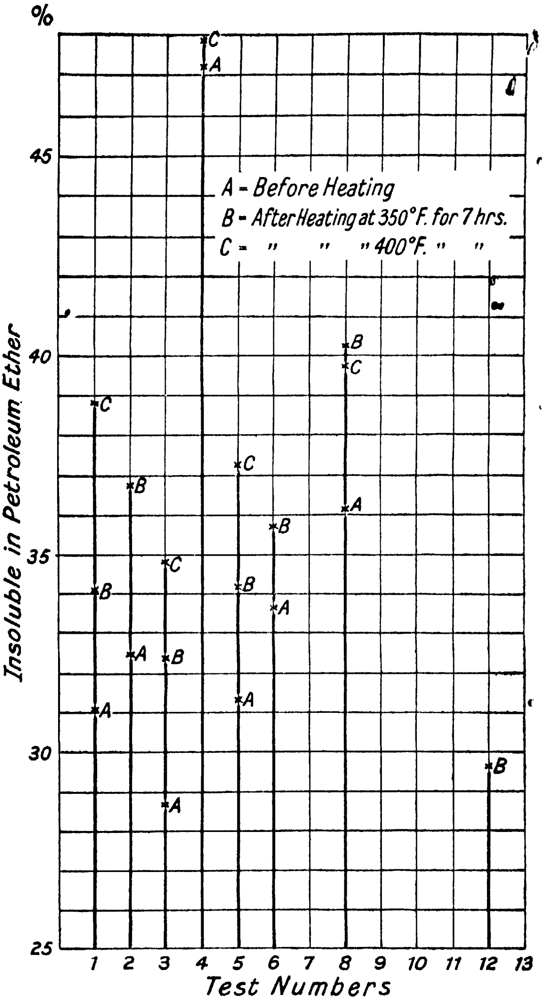


FIG. 13.—PER CENT. BITUMEN INSOLUBLE IN PETROLEUM ETHER.

8. *Fire-Point.*—There is nothing to be deduced from these figures.

9. *Insolubility in Petroleum Ether* (Fig. 13).—These figures are best demonstrated in columnar form, and are all fairly similar. No. 4 is exceptional in its results, but No. 6 is normal.

The apparent increase of asphaltenes with heating, as shown by the increased insolubility in petroleum ether, must be looked on as fictitious. Increased asphaltenes means, broadly, a more desirable bitumen, yet it is fully substantiated that prolonged heating tends to diminish the quality of the material. In this case it must be assumed that the increase is due to the rendering insoluble of a certain proportion of the malthenes.

10. *Solubility in Carbon Disulphide.*—There is nothing to be deduced from these figures, except that the samples consist of pure bituminous constituents.

11. *Fixed Carbon.*—There is nothing to be deduced from these figures.

12. *Ash.*—Only one figure was obtained.

13. *Appearance.*—Regarding the appearance of samples after heating, Abraham, in "Asphalts and Allied Substances," p. 485, gives the following comments on the "appearance surface aged indoors one week." Although he refers to bitumen under conditions somewhat different from those under discussion, there can be no doubt of the significance of the appearance in both cases being the same. "If bright and lustrous, it will indicate a perfect amalgamation of the constituents, also the absence of oily, greasy, and undissolved constituents. A lustreless surface is an indication of the presence of extraneous mineral or carbonaceous matter, or evidence that the constituents do not blend or amalgamate properly. If the surface appears greasy or wax-like, vaseline or paraffin-like bodies are present, since these

have the property of separating or 'sweating' from the bituminous matrix on standing."

DESTRUCTIVE HEATING.

Within the limits of the intention of this book the chief point of interest is the question of formation of *carbenes* as a sign and measure of damage by heat to bitumen. As will be seen, the matter is more properly included under this heading than that of "Moderate Heating," as it appears that very drastic overheating must occur before the percentage of carbenes appreciably increases.

This group of substances, soluble in carbon disulphide and insoluble in carbon tetrachloride, was recognised by Clifford Richardson[113] as being "evidently due to the severe treatment which the material has suffered in the course of its production at very high temperatures."

"A determination of the amount is only valuable as an indication of the care which has been used in the preparation of such pitches. In the best asphaltic residues from California petroleum the percentage of 'carbenes' has been found to vary from 7 to less than one-half of 1 per cent." They are probably formed by the cracking of paraffin and asphaltic hydrocarbon into both naphthenes and unsaturated hydrocarbon, the dangerous temperature being about 260° C.[107]

As has been already said, the carbene estimation is of little value, if any, in the case of bitumen manipulated as is customary, or even carelessly, in industry. (See also [183].)

AGEING OF BITUMEN.

The changes that occur after bitumen has been removed from its source may be negligible or great. Albertite and its relatives suffer no change; Trinidad asphalt rapidly hardens on the surface of the lake, whilst residual bitumens undergo a considerable and prolonged change after suffering the heating necessary for its production. This change is two-fold—a slow hardening due to the action of light and air on the residual oils remaining in the bitumen, and a slow and mysterious "settling down," of a nature that can only, and unsatisfactorily, be termed "internal molecular rearrangement." That this vague phrase is actually in the direction of correct interpretation is seen by the increase of the asphaltenes and melting-point, with the time.

The simplest method of observing the progressive change is the determination of the penetration, and a significant difference is found between tests and at the surface and at 3 mm. below the surface, the former being the lower, as might be expected. As there is a similar difference between the figures of the tests taken at the sides and nearer the centre, it would seem that there is a definite effect of relatively rapid cooling. That this divergence increases with age is evidence for the reality of the phenomenon.

This phenomenon of slow hardening with time has long been known, but the rate has usually not been indicated. The following figures have been obtained with a sample of residual bitumen:

TABLE IX.

PENETRATION OF AGEING RESIDUAL BITUMEN.

Time in Days.	*At Surface.*	3 *Cm. Below Surface.*	*Asphaltenes.*	*Fusion-Point (Degrees C.)*
0	46	—	31·5	56·0
7	42	45	—	—
43	38 (35 to 41)	43 (41 to 44)	—	—
205	25 (20 „ 30)	39 (36 „ 42)	—	—
487	23 (21 „ 26)	33 (30 „ 40)	38·9	58·3

For comparison, sample heated for seven hours at 204° C. showed increase on asphaltenes 31·1 to 38·8 This remarkable coincidence may well be fortuitous.

To compare with this, tests were made on a sample cut cold from bulk. The average penetration at the surface, from figures ranging from 42 to 35, was 39, a result equal to the ageing under the above conditions of thirty-four days. This, though in the right direction, is obviously anomalous, and is very characteristic of what frequently occurs when attempting to obtain strictly accurate and comparative figures from such substances.

Previous observations of the same phenomenon have led to the general views—namely, that the increase is due to oxidation, action of light and polymerisation,[114, 85, 52, 86] but it has not so far been suggested that one important factor in causing the hardening is the presence of paraffin wax or ceresine. It is to be expected that on sudden cooling this material solidifies to a super-cooled liquid which slowly changes to a more crystalline solid, comparably (and, of course, superficially so) to the change of liquid sulphur, first to the plastic form and finally to the crystalline. The proportion of wax or ceresine present, the degree to which it consists of a few or many members of its family, and the influence of colloids in the whole mixture, will all influence to an important degree the power of crystallisation and the time taken, and the completeness and normality of crystalline shape. It would appear to be very probable that the immediate surface hardening is due to this physical process, whilst the slow increase of general hardening is due to actual polymerisation as indicated by the increase of asphaltenes.

CORRELATION OF AGEING AND EFFECT OF HEAT.

An important advance towards the understanding of the production of coal, petroleum and bitumen would be made if it could be established how far the action of a relatively high heat in the laboratory during a short period of time was equivalent to the action of a much lower temperature during geological ages.

Highly significant work has been done on the conversion of cellulose to coal by Bergius, who obtained figures from chemical observations of the same order as those given by the geologists for the time of formation of the Coal Measures.

No work has been found, of the same nature, as to the comparable changes brought about in the laboratory and in nature with petroleum and bitumen; but a small step on the way is taken in the observation of the astonishingly exact parallel between the effect of heat on a sample of residual bitumen and its spontaneous ageing.

TABLE X.

CORRELATION OF AGEING EFFECT AND HEAT.

Time of Heating, in Hours.	*Penetration at 25° C., from Average Curve.**	*Days of Spontaneous Ageing.*
0	46·5	0
2	43	10
4	41·5	20
6·5	40	30
10	37·5	50
14	35	70

* Of curves obtained at 121° and 177° C.: they were not very different.

From these figures it is seen that under the conditions of experiment the change has been accelerated by heat, in the ratio of 1: 120.

RECOVERY BY SOLVENTS.

It is commonly stated that bitumen can be dissolved out of mixtures by means of chloroform and tested after the complete removal, by heat, of the solvent. This is yet another of those "accurate-inaccurate" statements that make the study of this branch of knowledge so troublesome and time-wasting, because no warning is given that the recovered material may be obtained almost unchanged or almost completely altered. Nor is any emphasis laid on the fact that the extraction with chloroform should be carried out in the minimum of light.

There are two sources of suspicion to be attached to this operation: first, the prolonged heating that is necessary to drive off the last portions of the solvent; and secondly, the complexity of the composition of the bitumen.

Trials were made with three solvents—chloroform, because it is commonly recommended; carbon disulphide, as being possibly more chemically inert; and crystallisable benzole, as being an almost pure, inert, single chemical substance.

A preliminary trial showed solubilities to be—

	Per Cent.
Benzole	99·13
Benzole followed by carbon disulphide	99·44
Carbon disulphide	99·50

The failure of benzole to dissolve the final 0·87 per cent. leads to the failure as a solvent for recovery, as is seen in the Table on p. 77.

From the figures, and others that have been obtained, it appears that successful recovery of bitumen primarily depends on the constitution of the bitumen itself; the purer the bitumen—that is, the less paraffin wax and the like that are present—the less changed is it by solution and recovery.

TABLE XI.

RECOVERY OF BITUMENS BY SOLVENTS.

Test.	*Before Extraction.*		*After Extraction with*					
			$CHCl_3$.		CS_2.		C_6H_6.	
Bitumen.	*C.*	*D.*	*C.*	*D.*	*C.*	*D.*	*C.*	*D.*
Ductility ..	78·5	+100	95	—	13	+110	6	50
Penetration	45	50	—	—	33	58	26·5	36
Fusion-point	55·5	54·5	67	—	67·3*	61·3*	70·8	63·3
Appearance	Dull	Bright	—	—	Dull	Bright	Dull	Bright

* After further treatment by admixture with water to drive off the carbon disulphide.

CHAPTER V

PHYSICAL AND CHEMICAL TESTS

THE various well-known tests are individually of no great value for the purpose of indicating the nature or quality of the substance examined: at best they are, separately, good sorting tests. But when considered together the importance of each is greatly increased by the combined illumination that results, and very little doubt remains as to the suitability of the material for a particular purpose or the fulfilment of a specification of definite demands.

Together with these practical requirements is the less immediate but more important question of the complete and intimate understanding of the composition of bituminous substances. This is, at present, far from being fully elucidated, and the nature of the difficulties of the investigation has been indicated elsewhere, but the key to the understanding of their nature probably lies in the realisation that they consist of a very complex mixture of substances holding colloidal matter of high carbon content in suspension, this whole being itself a colloidal suspension in petroleum oils.

PHYSICAL TESTS.

From what has already been shown, it will be seen that tests in this category depend on the graduated variety of the material's constituents and must necessarily be arbitrary, not only as regards the moment that they are considered to have been fulfilled, but also in the manner in which they are carried out.

Specific Gravity.—There is little to record about this determination, except to draw attention to the usefulness of Hackford's apparatus, a description of which has, as yet, not been published.

It consists of a specific gravity bottle, open at both ends, to which are attached, by ground glass joints, two tubes to facilitate filling, and to prevent the entry of anything but the material to be tested during the contraction on cooling. The dimensions are shown in Fig. 14.

The bottle is standardised by water at a known temperature, evaporation during weighing being prevented by closing the ends with the smallest size microscope cover glasses; these may be retained in their place by the surface tension of the water or by the assistance of a trace of grease.

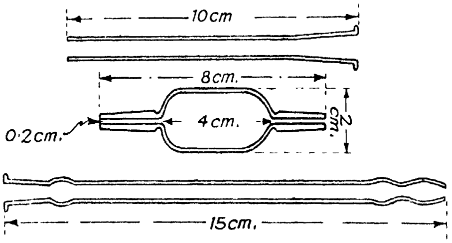


Fig. 14.—Hackford's Specific Gravity Apparatus.

After this, the material to be examined is sucked into the bottle by the mouth or a pump and allowed to cool to the correct temperature. The tubes are removed and the bottle and contents are weighed, and the comparison with water made in the usual way. With very little practice results concordant to two in the fourth decimal place can be obtained.

Fusion-Point.—This test, which is usually the first to apply to any substance for characterisation, identification, or establishment of purity, at once shows up the troublesome nature of these substances. Like all mixtures, they have no definite melting-points, but gradually soften as the temperature rises. Therefore, the terms "melting-point" and even "softening-point" have little true significance, so that "fusion-point" has been taken here to designate the temperature at which the material is arbitrarily considered to have become soft.

One of the earliest methods, if not the earliest, of ascertaining the fusion-point is that of *Krämer and Sarnow*[115] (1903). It still survives, though somewhat modified in its details, but it has not been accepted as a standard. It consists in melting the sample at about 150° C., introducing a quantity of about 5 mm. height into a tube 6 to 7 mm. wide and, when solid enough, bringing on top of it 5 gr. mercury; this, by its weight, breaks through the material when it is carefully re-heated in a water bath; the temperature at which this happens is taken to be the fusion-point. Repeated trials give results within 1° C.

This has been modified[116] by substituting, for the downward weight of mercury, the upward thrust of the water of the water bath in which the sample is immersed to a definite depth; by this means results are reproducible to within 0·5°. Other minor changes have been made,[117-120] including the application of electricity, which rings a bell by contact of the mercury after its passage through the sample, turns off the gas heating the water bath, and allows a flood of cold water to pass and cool the apparatus for the next test[121]—a regular engineer's job. Electricity can also be used for heating the water bath at a regular rate.[21]

The *cube method*, in oil and in air, and the *ball and ring* method were compared[122] (in 1914), the latter being at that time regarded as likely to be acceptable when thoroughly standardised. In 1915 they were again compared,[123] and in 1916 the ball and ring method was specified in detail.[124, 125] Although this is now adopted as a standard method in both England and America, it is of interest to notice other suggestions that have been put forward.

The *Richardson ball method* consisted in heating the sample, as a ball the size of a pea, on a microscope cover glass floating on the surface of mercury. The temperature of the latter was raised at a uniform rate, and the thermometer was read when the ball had collapsed so far as to form a sphere with its reflection.

The *General Electric Co.'s method* was to build up, film by film, a cylinder of the material to be tested round the bulb of the thermometer. This cylinder was trimmed and the whole heated in a test tube, and the temperature was noted when the cylinder slipped off and fell to the bottom of the tube.

These two were compared with the Krämer-Sarnow and ball and ring methods,[126] the last being considered good, but not suitable for factory use.

A *drop method* was devised where a sample was most carefully heated in a special apparatus, so that when melted the substance dropped through a hole.[127] Another[128] consisted in the sample being held in a tiny container which was in touch with the bulb of a thermometer by means of mercury in contact with both. At a particular temperature the sample dropped through a hole in the bottom of the container.

The *tap method*, as it might be called, is unusual in its operation.[200] The sample is softened (not melted) sufficiently to be moulded into the bore of a barrel of a tap of a tube which is supplied with air at a known pressure. The temperature of the tap is slowly raised, and a sudden drop in the air pressure indicates the moment when the sample has become so soft that it has been blown out of the bore of the tube. Repeated tests on a gilsonite gave results within two degrees.

Another form of test[178] is, in principle, not unlike Kirschbaum's test for adhesiveness. A ball, set in the substance to be investigated, is connected to one end of a balance; to the other is attached an excess weight and a pointer. The latter inscribes on a clockwork-driven drum the movement permitted to the ball during regularly increased temperature. These curves are characteristic for the material.

From the number of the tests and the ingenuity that has been expended on them, it is obvious how useful the property is, and how troubled investigators have been over its establishment. Now that the ball and ring test has been adopted as the standard method, there is likely to be a lull in work in this direction; but even this test has its inconveniences, and there is still room for further inventive thought.

Consistency.—From a technical standpoint, this (with surface tension) is another important property of bitumen, as on it also depends the immovability of asphalt mixtures of all kinds.

The term " consistency " is found in the literature on the subject as an alternative to hardness, though usually —and desirably—it covers those properties of the substance revealed by means of the penetrometer, ductility machine and the rest.

Its best definition is, perhaps, "the degree of firmness," of the material, whilst the property of *hardness* is even more difficult to characterise. It might be "resistance to deformation," though this has more to do with shear and viscosity; or as "resistance to shock," which is, more truly, resilience; or "resistance to blows without fracture," which is, more accurately, a definition of brittleness. Doubtless it is on account of such indecision that "hardness" is seldom, if ever, met with, and "consistency" is more often used.

A test which probably most nearly represents this property in its general form is the following. A wedge-shaped sample is supported by its broad end in a water bath, and its behaviour, which may be very characteristic, is noted during slow rise of temperature. It may shear or bend, and its movement is measured by sighting against lines on the containing beaker.

Viscosity is usually measured in the laboratory by the time taken for a given volume of a liquid to flow, at a given temperature, from a standard instrument, which in this country has been devised by Redwood, in Germany by Engler, and in America by Saybolt.

These instruments have not been in complete favour for use with bituminous substances, on account of a variation of results of 5 per cent. and a limit as to temperature range,[39] an objection that has now been overcome in this country by the adoption, as standard, of a modified Redwood No. II. viscometer.

As it may sometimes be more desirable to express this arbitrary unit of time in terms of absolute viscosity, there has been worked out an equation for the purpose,[130] not without some trouble, as the subject is one of notorious difficulty. (See, for example, [168].)

The equation obtained is:

$$\text{Kinematic viscosity} = \frac{\text{Absolute viscosity}}{\text{Density}} = \frac{\mu}{\gamma}$$

$$= At - \frac{B}{t},$$

where t = time of discharge in seconds.

A = a constant = 0·00213 for the Saybolt instrument.
= 0·00147 for the Engler instrument.
B = a constant = 1·535 for the Saybolt instrument.
= 3·74 for the Engler instrument.

This equation fails above the critical velocity of flow of about $800 \times \frac{\text{Kinematic velocity}}{\text{Diameter of tube}}$ when turbulent flow begins. As this figure is exceeded by water, Ubbelohde's equation for the Engler instrument is wrong.

The suggestion that the name of the unit of absolute viscosity should be the "poise," after Poiseuille,[131] who did such valuable pioneer work on the establishment of the theory of the matter, has been adopted. It so happens that the centipoise is almost exactly the viscosity of water at 20° C., hence the absolute viscosities in centipoises are specific viscosities referred to water at 20° C. as standard.[112]

The change of viscosity with temperature has valuable significance when comparing samples of bitumen. (In the following figures for sample C (Table XII.) the upper ones have been approximately extrapolated, but may actually reach a figure very much higher.)

The viscosity of mixtures has not the simple relation to that of the constituents that might be expected. It is found[132] that it is the logs. of the viscosities, in poises, that are additive, but that the larger the difference of the viscosities of the constituents the larger will be the deviation from this rule, the true value being less than the calculated. For equal differences in the values for the compounds the error increases as the viscosity of the lighter component decreases, the true viscosity being greater than that calculated.

It is remarkable that the viscosity (as indicated by a rotatory cylinder) is greater during rising temperature than when the temperature is falling.[133] This hysteresis is tentatively explained by change from "plastic" to "elastic" deformation.

TABLE XII

VISCOSITY: VARIOUS SAMPLES OF RESIDUAL BITUMEN.

t° F.	*A.*		*B.*		*C.*		*D.*	*E.*		*F.*		*G.*		
450	—	—	—	—	100	133	—	—	—	—	—	—	—	—
400	268	250	355	350	—	—	261	*200	188	525	524	250	274	260
350	606	600	1,628	1,625	300	326	835	600	607	1,200	1,195	600	588	—
300	1,803	1,750	6,540	6,500	1,000	978	2,360	1,800	1,764	5,325	5,320	750	1,940	1,764
250	—	—	—	—	2,100	—	—	—	—	—	—	—	—	—
200	—	—	—	—	(4,000)	—	—	—	—	—	—	—	—	—
100	—	—	—	—	(9,400)	—	—	—	—	—	—	—	—	—
0	—	—	—	—	(21,000)		—	—	—	—	—	—	—	—

NOTE.—D is purer—has less wax than C.

One effect of the presence of finely divided mineral matter has already been described, but reference must be made here to the first attempt to represent this mathematically for practical use. Even though the work refers to the stiffening of coal tar,[134] there can be no doubt that the same general laws hold for bitumen. The results are the more remarkable as it has been found that the fillers, of which no particles were larger than 0·01 inch diameter, all gave the same results, whether they consisted of granite dust, limestone, or cement, which is in some contradiction to the preference given to one filler or another in industrial works.

---

* An old sample.

Viscosity was determined with Hutchinson's tar tester (see later, p. 95), and the increase due to the addition of filler was

$$V_F = V^x \quad . \; . \; . \; . \; . \; . \; . \; . \quad 1$$

where V = consistency of the tar alone,

V_F = ,, ,, ,, and filler at the same temperature.

x varies with the percentage of filler added, in such a manner that

$$x = KF + 1 \quad . \; . \; . \; . \; . \; . \; . \; . \quad 2$$

where F = percentage of filler,

K = $8{\cdot}5 \times 10^{-3}$.

From the combination of equations 1 and 2 there is obtained

$$F = \frac{\log. V_F}{\log. V - 1} \div 8{\cdot}5 \times 10^{-3},$$

an equation giving the percentage of filler necessary to increase the viscosity from V to V_F.

Penetration, the length of vertical travel of an entrant body into a sample at a given temperature and in a given time, has received a great deal of attention, as it is a test that is easy to apply, and one that gives a simple method for ascertaining the quality of a sample for a particular purpose, and of comparing and classifying samples.

Here, again, is to be found that state of arbitrariness that pervades this whole subject, resulting, in this case, from the lack of purity of phenomenon. The penetration of a solid into a viscous liquid is not a simple matter. The resistance to the entering needle consists of friction at the contact of the two materials, coupled with displacement and flow of the sample; and it depends on the arbitrary determination of the width and thickness and shape of the plunger (used with any particular sample) as to what are the relative magnitudes of these resistant forces. Even the size of container is of importance[135]: it has been found that the smaller the container the lower is the penetration, a change that is doubtless connected with increased difficulties of the adjustment of the volume of the sample to the volume of the entering solid.

Like the rest of the tests, conditions have to be carefully controlled, but the following figures are of interest as indicating how far results may vary when varying these conditions.

Modification of the temperature of the test gives the following figures:

TABLE XIII.

PENETRATION TESTS WITH MODIFIED TEMPERATURE

	Penetration.	
t° C.	*Sample C.*	*Sample E.*
25	45·0	22·0
20	27·0	16·5
15	18·0	12·5
10	12·5	9·5
5	9·0	7·0
0	7·0	5·0

The changes in results that are found when modifying temperature, weight, and time are the following:

TABLE XIV.

PENETRATION TESTS WHEN MODIFYING TEMPERATURE, WEIGHT AND TIME.

Sample.	0° *C.*				25° *C.*	46° *C.*	
	100 *Grs.*		200 *Grs.*		100 *Grs.*	100 *Grs.*	50 *Grs.*
	5 *Secs.*	60 *Secs.*	5 *Secs.*	60 *Secs.*	5 *Secs.*	5 *Secs.*	5 *Secs.*
C	5	10	10	17	45	Too	soft.
E	5	7	7	13	22	134	82

In the usual penetrometers the plunger has long consisted of a needle, known as Parabola "Sharps" No. 2,[136] of R. J. Roberts, Redditch, England. It was found necessary soon after its adoption to exercise much care in the selection, owing to lack of strict uniformity of the shape, and examination under the lens was recommended in order that only those should be used that coincided with the standard needle—not specified.

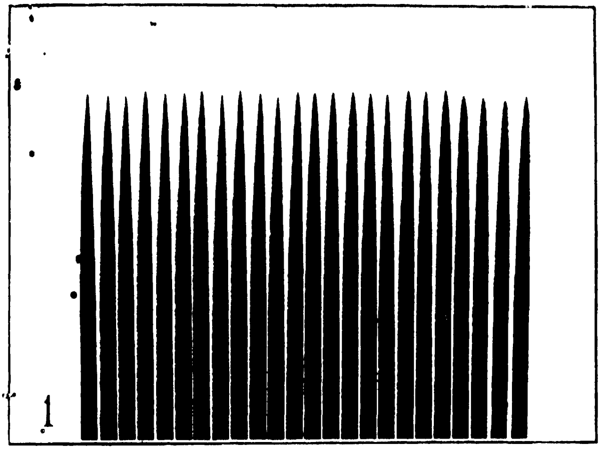
In 1916 came a definite attack on the No. 2 needle,[137] when it was shown how out of seventy-two needles only twelve could be used and of these only five gave concordant results. A needle consisting of a steel drill rod of definite dimensions and polish, and with a ¼ inch taper to a point, was recommended as giving results close to existing standards and simple to reproduce accurately (see Plate I.).

By 1920, however, it was realised that the point of this needle was easily damaged, so, again with no important change in numerical results, it was finally standardised[189] as being truncated to a blunt end of 0·15 mm. diameter.

This idea of the blunt needle had been arrived at by Colonel Crompton as the result of work starting as far back as about 1909, the result being the employment of standard steel wire of square section of 1 mm. edge, and also of wire of circular section of about 1·3 mm. diameter.[195] No published work of his in conjunction with the National Physical Laboratory is available.[138]

A further possibility of variation was found to be in the lack of facilities in the details of adjustments of the instrument, particularly when employed in the factory. The first instrument for general use was that of Dow, produced in 1903, and further improved upon by Richardson and Forrest. These various modifica-

PLATE I.



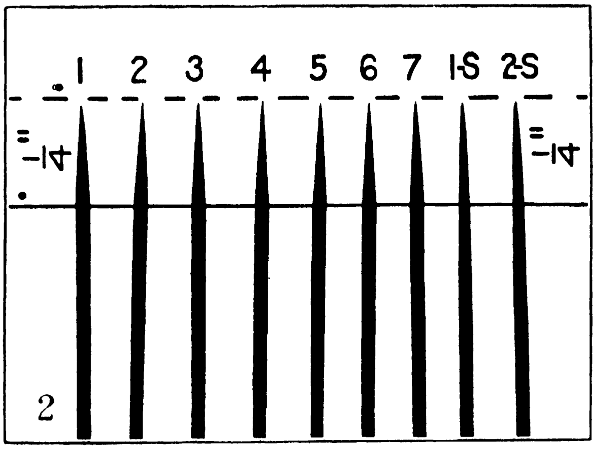


Fig. 1.—Direct Enlargement of a Package of No. 2 Sewing Needles, showing the Variations in Shape.

Fig. 2.—Direct Enlargement of Penetration Needles, showing the Comparison between Two Standard Needles (1 S, 2 S), and Seven Needles of the New Type prepared by the Authors.

tions,[139-141] and the reasons for their introduction, are fully described in the original papers referred to, and need not be repeated here.

Other closely connected sources of variation occur in the setting of the indicator, the personal error in the operation of the clamp controlling the moving part exactly to time, and in the accuracy of the stop watch or metronome, the second being considered to be of greater influence than that of the variability of the shape of the needle.[141] For this reason automatic instruments have been constructed and patented from the beginning, but none appear to be so free from objection as to command universal adoption.

The members of this type of apparatus fall naturally into two classes, and it is remarkable how similar to one another are the individuals of each group. The illustrations, taken from the various patent specifications, are sufficient to show the general nature of the instruments.

The older and more complicated type may, for convenience, be called the " long arm " type. This comprises Bowen's (1893), Dow and Griffith's (1894), and Hall and Marriott's (1919). The newer form, to be named. perhaps, the " vertical drop " type, is exemplified by Rawstron's (1910), Hutchinson's (1911), Mohr's (1914), and Howard's (1917).

Bowen's instrument[142] (Plate II.) was based on a wooden model of his, the first to be devised (in 1888) for this purpose. It was hand controlled, and contained all the essential details that are considered to be desirable to-day. It shows remarkable insight and understanding of the requirements of the problem.

Dow and Griffith's instrument[143] (Plate III.) was controlled electrically by a pendulum.

Hall and Marriott's[144] apparatus (Plate IV.) has a mechanical timing device to control its movement.

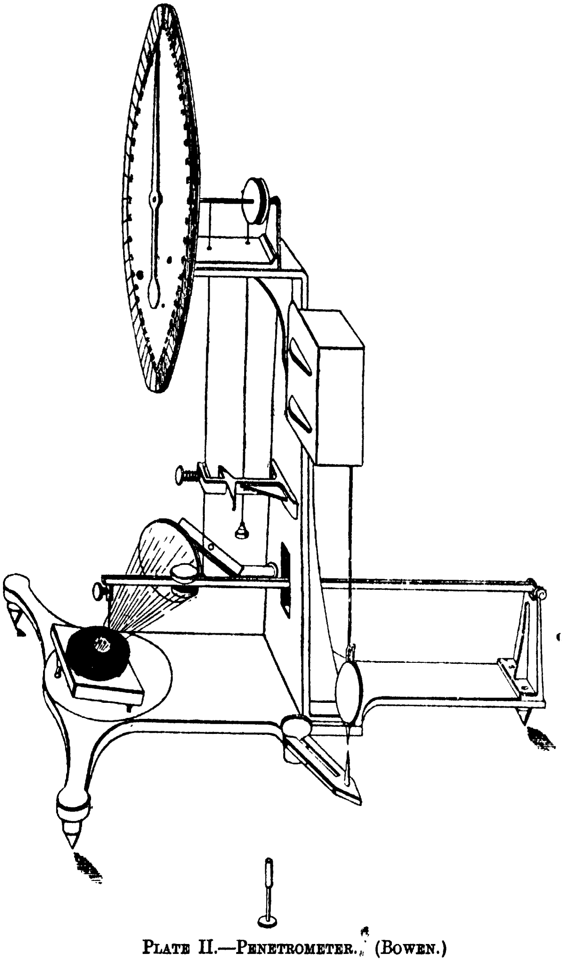


Plate II.—Penetrometer. (Bowen.)

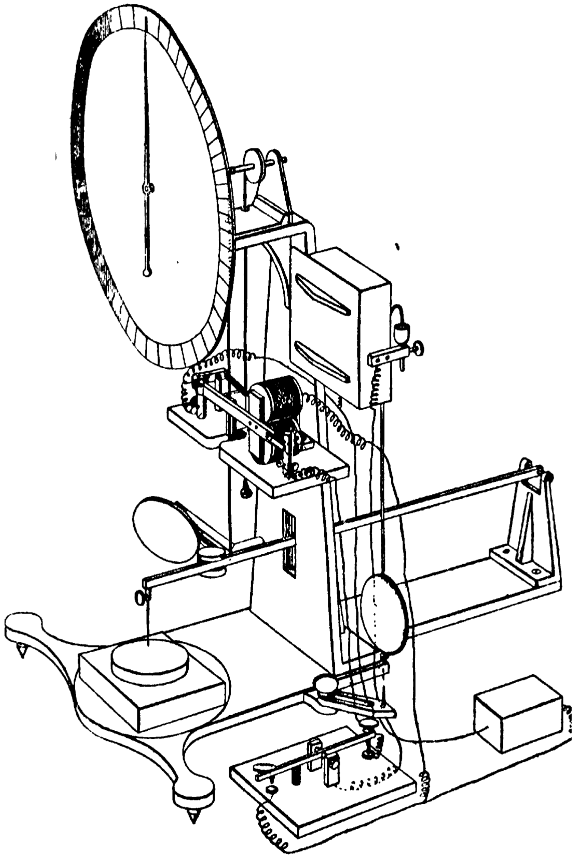


Plate III.—Penetrometer. (Dow and Griffith.)

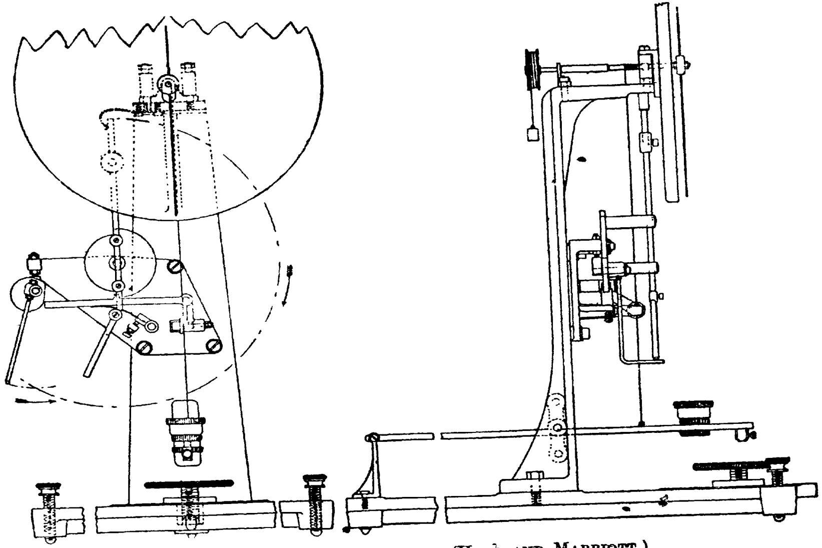


Plate IV.—Penetrometer. (Hall and Marriott.)
(*Reproduced by permission of the Controller of H.M. Stationery Office.*)

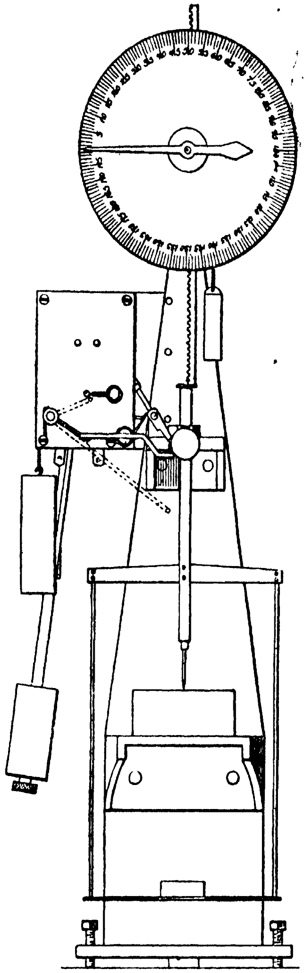


PLATE V.—PENETROMETER. (RAWSTRON.)

Rawstron[145] controlled the fall of the vertical rod by a pendulum and clockwork (Plate V.).

Hutchinson,[146] (1911) used a wheel, over which passed a string; to this, at one end, was attached a selected plunger and at the other a pan for weights partially counterbalancing the plunger. The depth of penetration was indicated by a Dow scale (Plate VI.).

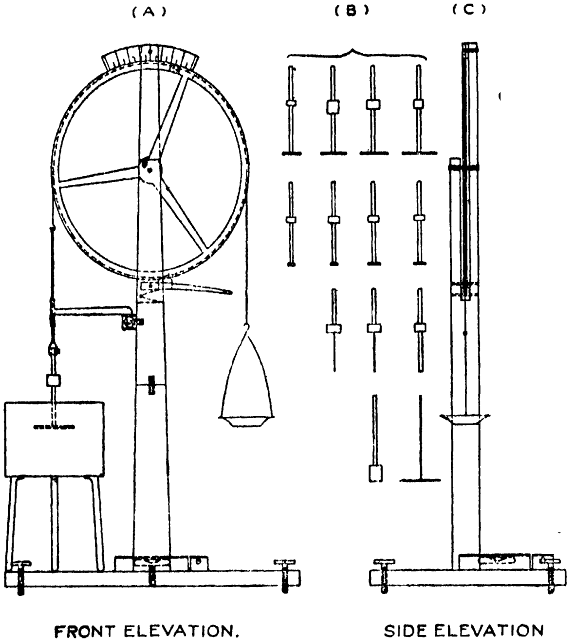


PLATE VI.—PENETROMETER. (HUTCHINSON.)
(Reproduced by permission of the Controller of H.M. Stationery Office.)

Mohr (1914),[141] describing the instrument used in the Standard Testing Laboratory, Board of Estimates and Appointments, New York City, claims results so exact as to permit of differentiation between various needles. It consists of a vertical rod held and released by electromagnetic relays from a timing mechanism.

Howard (1917) also put forward[147] a vertically moving instrument, in which an electromagnetic clamp is automatically controlled (Plate VII.).

The various papers to which reference has been made contain much valuable information; but the effect of variation of the smaller details of the test has been especially examined in an excellent paper by Hubbard and Pritchard.[148] (See also [149].)

A drawback in all these instruments is that when used for a wide range of substances different loadings of the needle are necessary. To avoid this and to bring all such tests into one continuous and inter-comparable series of observations an instrument was invented simultaneously and independently by Crosby and Abraham,[39, 150] and is known as the *Consistometer.* Here, by the use of plungers of graded dimensions, the hardness or consistency is expressed by the cube root of the grams necessary to cause a surface of 1 sq. cm. to be displaced at a uniform speed of 1 cm. per minute. Thus, the number of grams is directly proportional to the volume displaced.

The principle of the travelling plunger is manifested by *Hutchinson's Tar Tester*, an instrument that is widely used, but which does not appear to have any scientific basis for its dimensions. This instrument, whilst being referred to as an instrument of precision, has been modified in America,[151] so that a smaller amount of the material to be tested is required (thus facilitating temperature control) and cleaning is rendered easier.

Ductility.—The capacity for being drawn apart without fracture is a test that has been described as "a measure of surface tension,"[152] though it is more than that. Its significance lies, in part, in its dependence on the presence

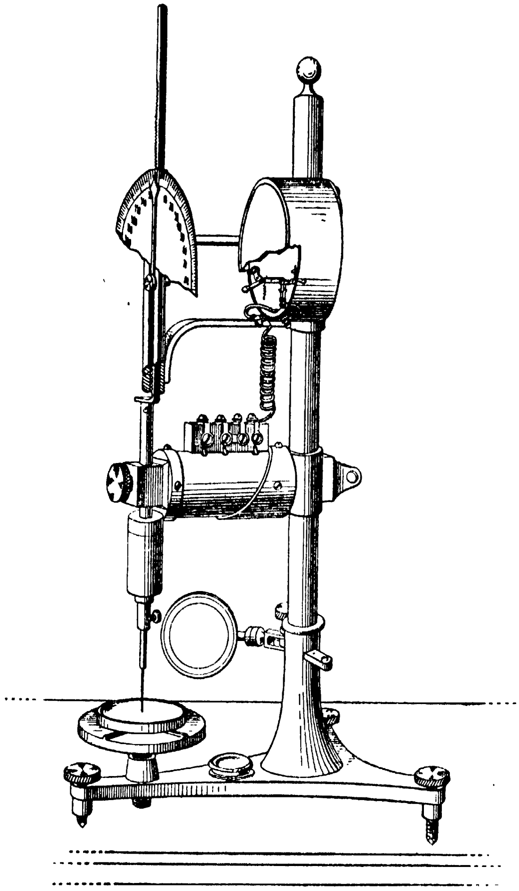


Plate VII.—Penetrometer. (Howard.)

of resins and unchanged oils; when, for example, these are oxidised to the brittle asphaltenes, ductility rapidly diminishes.[37] Its value has been called in question by the assertion that the ductility of a roadway bitumen is about 0 at 0° C.—that is to say, it is quite brittle, and yet the road does not break up under the first shock or drag. This criticism would be valid if it were contended that the stability of an asphalt road depended solely on the ductility of its bitumen. In the writer's opinion, the test is undoubtedly of importance as an indication of the nature of the material, as it is considerably more sensitive than is the penetration test, though neither is of much fundamental value apart from other tests. It indicates the likelihood of the damage that may be done by "inadvertent overheating," and constitutes a valuable protection to the buyer against "adjustment" of an overheated charge, as it is probably impossible that both the penetration and the ductility can simultaneously be restored after being so damaged. This is seen in the following figures obtained from a sample of residual bitumen, C, which was kept at a little below 200° C. for five hours, during which time much sulphuretted hydrogen was evolved and a distillate was collected that smelled somewhat of cracked oil.

TABLE XV.

TESTS ON A SAMPLE OF OVERHEATED RESIDUAL BITUMEN.

	Ductility, Average.	*Penetration.*	*Solubility in Carbon Disulphide.*
Unheated material ..	63·0	45	99·6
Residue, after testing..	3·0	50	98·8
Residue, mixed with distillate	3·5	100	98·7

The test on a sample is most properly carried out in triplicate, and the utmost care must be taken to follow the directions of the test in every detail. Even then irregularities occur whereby two results of the three are closely coincident and the third may be considerably divergent. A minute bubble, a tiny fragment of mineral matter, irregularity of movement of the travelling carriage, may be the cause, or simply local change occurring during the preliminary heating of the sample. (See also [153].) This sensitiveness of bitumen to heat is well seen when comparing the results of a sample prepared in the ordinary fashion with that cut cold from a block of the material. Here, of course, irregularities may occur, but not always, from enclosed bubbles of air and of water.

The results with some grades of bitumen are +100, and more significance can be obtained by reducing this either by doubling the speed of the machine[152] or by lowering the temperature of the test.

The sensitiveness of this test has led to the carrying out of much investigation work for the proper understanding of the factors that control the accuracy of the test. These may be grouped as being associated with the preparation of the sample and with the machine on the one hand and with the conditions of test and with the material tested on the other.

The first group of conditions includes the mode and time of heating of the sample preparatory to pouring into the mould and of the cooling in the mould, the shape of the thread and the method of trimming the sample before testing. The results may be summarised as follows:

1. The temperature and duration of heating the samples have a definite effect on the results.
2. Preliminary warming of the moulds and the order of their filling (as affecting the temperature and viscosity of the bitumen) have no effect.

3. The time of cooling has some influence on the results, but this is of no serious importance within the short periods of laboratory conditions. A period of rest of several weeks and more would certainly result in a greatly lowered figure.

4. The trimming of the sample with a hot or cold soaped razor is better than a common knife, but an amalgamated brass plate is to be preferred.

5. Most unexpectedly it was found that quite large variations, even up to four times, in the size and shape of the cross-section of the test piece did not cause nearly such great differences in results as were to be anticipated from the proportional deviations from the standard of 1 sq. cm. Certainly any very small variations in the dimensions of the moulds will have no effect on the results. The figures obtained are given in Table XVI., but, like most scientific measurements connected with bitumen, they are not free from anomaly, and only show clearly the direction of argument rather than consistent and exact proof.

TABLE XVI.

EFFECT OF VARYING DIMENSIONS ON DUCTILITY MOULDS.

Shape of cross-section	1 to 6 11 to 19	8	9	10	9+10	X	Y	Z	—	—	—
Width ..	—	0·97	0·90	1·00	1·00	1·10	2·05	1·00	—	—	—
Height ..	—	0·91	0·93	0·76	1·78	0·45	1·00	1·78	—	—	—
Area ..	0·99 to 1·03	0·88	0·84	0·76	1·78	0·49	2·05	1·78	0·65	0·86	0·92
Ductility of various samples ..	—	69	—	—	67	—	—	—	—	—	—
	—	62	—	—	73	—	—	—	—	—	—
	74	—	—	—	—	—	—	73	—	—	—
	75	—	—	—	—	43	+100 (? 150)	71	—	—	—
	79	—	—	—	—	73	+100 (? 150)	100 (? 110)	—	—	—
	—	—	—	—	—	37	—	74	37	9	70
	57	—	—	—	—	54	+100	63	—	—	—

In addition it is seen that the ribbon-shaped cross-section leads to higher figures than does the upright-shaped.

It is interesting to note that during the drawing out of the thread very little material is contributed by the mass of material in the ends of the moulds. A straight line, drawn across the ends of the mould, was observed to advance into a bow shape by at most 5 mm. A comparison between a sample treated in the ordinary way and one cut cold from the solid block showed the following results:

Temperature of Test.	*Normal Sample.*	*Cut Samples.*
18° C.	15·0	9·5
25° C.	62·5	19·5

Considering the last figure of 19·5 is an average of 16, 18, and 24·5, it is clear that preliminary heating is not alone responsible for the irregularities of results that are found, and that the material cannot be homogeneous. This is actually seen in the photograph (Frontispiece) of the conchoidal fracture of a sample of residual bitumen, where small hollow spaces, whether of air or water, are clearly visible.

6. There is no connection between irregular results and the order of contact between the threads and the bottom of the ductility machine, though such contact is undoubtedly detrimental.

7. Irregular results sometimes occur without such visible cause, as the attachment to the thread of a tiny bubble or speck of solid matter, or the inward curvature of the surface of the test piece resulting from contraction on cooling after being trimmed; such inexplicable figures can only come from irregularities in the quality of the bitumen due, possibly, to local changes caused during the preliminary heating. Lack of homogeneity sometimes becomes apparent by the formation of a visible lump on the thread.

The effect of conditions of test is of considerable interest.

The effect of temperature of test on sample C of Mexican bitumen prepared in the usual way is shown in the following table:—

TABLE XVII.

Ductility Tests with Modified Temperature.

	Normal Samples.		*Cut Samples.*	
t° C.	*Average Figure.*	*Range of Variation of Individual Results.*	*Average Figure.*	*Range of Variation of Individual Results.*
18	14·5	3·0	9·5	2·0
20	20·0	5·5	12·5	2·5
22	22·5	9·5	15·0	3·0
24	50·0	13·5	19·5	4·5
25	61·5	30·0	19·5	8·0

Included for comparison are the results from bitumen cut to shape and tested without heating; these will be further referred to later.

If the figures for the range of ductility be plotted against temperature, a sharp kink is found at 24° C.

It was found also, but further substantiation is required, that the ductility of a blended bitumen is as low as, or lower than, that of any of the constituents, if these do not vary greatly among themselves.

A modification of this test is the *tensimeter* of Abraham,[21] which works vertically in a bath of the same specific gravity as the material being tested, and is provided with a dynamometer. Maximum tensile strength occurs usually when ductility is 0—*i.e.*, just when plasticity disappears and gives place to brittleness

—a fact of significance to asphalt roadmakers. There appears to be no connection between hardness and tensile strength. The mould consists of two halves of a completely closed container, which can be drawn apart in the usual way, thus avoiding several troubles associated with the usual ductility mould.

The *flow test* may be found to be useful in the field or at the works, but has had the drawback that the accurate preparation of the cylinders is not easy. This is got over very simply by the use of copper tubes,[154] clipped in position in the usual grooved plate. The distance travelled is measured after a flow of about four or five inches, when a difference of 5 per cent. from the standard may be considered to be unsatisfactory.

Adhesion.—The direct measurement of this important property is not yet soundly established. In principle it consists in measuring the force necessary to draw apart two surfaces between which the sample to be tested has solidified. This is again a purely surface action, so that the more the film exceeds molecular thickness, the more is the test vitiated by the introduction of the phenomenon of ductility.

A method has been described,[128] in which two brass discs, 1 inch in diameter, are pressed firmly together after the sample has been "smeared on." One is held immovable, while to the other is fixed a cord which passes over a pulley and is attached to a small pail. Into this shot are poured regularly at a rate of 2,250 grs. per minute and the weight noted when, at 20° C., the plates are pulled apart.

The further tests of Osborn and Kirschbaum are readily available,[21] the former of which is a kind of lubrication test.

Another method[129] is to melt the sample (the weight before and after heating giving a measure of volatility) into a split cylinder and pull the halves apart in a dynamometer. If the material pulls away from the crucible, internal cohesion is greater than adhesion; if the material breaks about the middle the contrary is the case. Inspection of the fraction shows the presence of air bubbles.

CORRELATION OF PROPERTIES.

It is of interest and importance, both for scientific and practical purposes, to determine whether and how far one property varies regularly with another, or is entirely independent of it. This subject requires more attention to be paid to it than has already been given; but for a truer understanding of the nature of bitumen the direction of the work to be done is indicated here.

CORRELATED TESTS.

Table XVIII. shows how far the properties of bitumen are interconnected. In some cases clear correlation is apparent, sometimes this is doubtful, but more frequently there is no traceable connection between the figures obtained.

Of the ten properties which have been compared with each other (some of which, when dealt with in two sections, have given contrary indications) there are of

	Per Cent.
Obvious correlation	42
Doubtful „	7
No „	51
	100

This high percentage of independence is remarkable, particularly as it includes such expected relationships as penetration and loss on heating; except in one case flash-point and fire-point do not show regularity with any other property, not even with one another.

TABLE XVIII.

Summary of Correlated Properties.—A.

Number of Single Test.	1.	2.	3.	4.	5.	6.	7.	8.	9.	11.
Test.	*Specific Gravity.*	*Fusion Point.*	*Penetration.*	*Ductility.*	*Viscosity.*	*Loss on Heating.*	*Flash-Point.*	*Fire-Point.*	*Insolubility in Petrol Ether.*	*Fixed Carbon.*
1. *Specific Gravity:*										
Relationship	—	*	*	‡	*	‡	‡	‡	*	‡
Number of correlation test		1	2		3				4	
Figure		15	16		17				18	
2. *Fusion-Point:*										
Relationship		—	*	*	*	*	‡	‡	*	*
Number of correlation test		—	5	6	7	8			9	10
Figure		—	19	20	21	22			23	24
3. *Penetration:*										
Relationship			—	*	*	‡	‡	‡	*	
Number of correlation test			—	11	12				13	
Figure			—	25	28				29	
Ductility:										
Relationship			—	—	*	‡	‡	‡	*	
Number of correlation test				—	14				15	
Figure				—	30				31	

5. *Viscosity*:										
Relationship					—	*	‡	‡	‡	†
Number of correlation test					—	16				17
Figure					—	32				33
6. *Loss on Heating*:										
Relationship						—	*	‡	‡	*
Number of correlation test						—	18			19
Figure						—	34			35
7. *Flash-Point*:										
Relationship							—	‡	‡	†
Number of correlation test							—			20
Figure										36
8. *Fire-Point*:										
Relationship									‡	†
Number of correlation test										21
Figure										36
9. *Insolubility in Petrol Ether*:										
Relationship									—	*
Number of correlation test										22
Figure										37
11. *Fixed Carbon*:										
Relationship										—
Number of correlation test										—
Figure										—

* Obvious correlation. † Doubtful correlation. ‡ No correlation.

The materials examined, together with their chief properties, were the following:

TABLE XIX.

Properties of Bituminous Substances and Mixtures.

No.	*Material, Sample Nos. and Proportion.*	*Specific Gravity.*	*Fusion-Point, Degrees C. (Ball and Ring).*	*Penetration.*	*Ductility.*	*Viscosity,* 204° *C.*	*Loss on Heating, 7 Hours,* 204° *C.*
	Bitumen.						
1	4,133	1·049	55·5	45	97	133	0·84
3	6,189	1·026	53	45	+100	268	2·20
4	6,190	1·074	85	18	3·75	355	3·05
5	6,194	1·014	56	34	+100	274 260	0·89
6	6,192	0·989	77	30	3	524	1·25
	Flux.						
7	6,251	—	83	33	3·5	—	—
8	—	1·051	65	22	14	188	0·22
	Bitumen E.						
9	1+ 10% 17	—	53	67	+100	110	0·44
10	1+ 10% 6	—	57·5	45	44·5	175	1·23
11	1+ 10% 7	—	56·5	48	46	—	—
12	3+ 10% 17	—	48	86	+100	187	1·89
13	3+ 20% 6	—	54·5	50	94	282	0·29
14	3+ 20% 7	—	—	—	—	—	—
15	8+ 10% 17	—	60	40	48	165	0·29
16	5+ 10% 17	—	51·5	54	+100	154	0·83
	Flux Oil.		*Flash-point Degrees C. (Closed).*			*At* 140° *F.*	
17	6,385	0·969	210	—	—	2,920	1·35
18	6,245	—	308	—	—	332	—
19	6,246	0·921	248	—	—	292	0·78
20	6,247	0·929	197	—	—	535	0·72
21	6,424	0·947	130	—	—	475	—
22	6,534	—	85	—	—	48	—

In the following curves samples Nos. 4 and 6 will be seen to show anomalies and irregularities; No. 4 in connection with the specific gravity—viscosity (Fig. 17), and loss on heating—fusion-point (Fig. 22) relations; and No. 6, which has all the properties of a blown bitumen, in connection with the following: specific gravity—fusion-point (Fig. 15), specific gravity—penetration (Fig. 16), loss on heating—fusion-point (Fig. 22), carbenes—fusion-point (Fig. 23), fixed carbon—fusion-point (Fig. 24), loss on heating—viscosity (Fig. 31), fixed carbon—viscosity (Fig. 32), and loss on heating—fixed carbon (Fig. 34). In both the specific gravity—carbenes

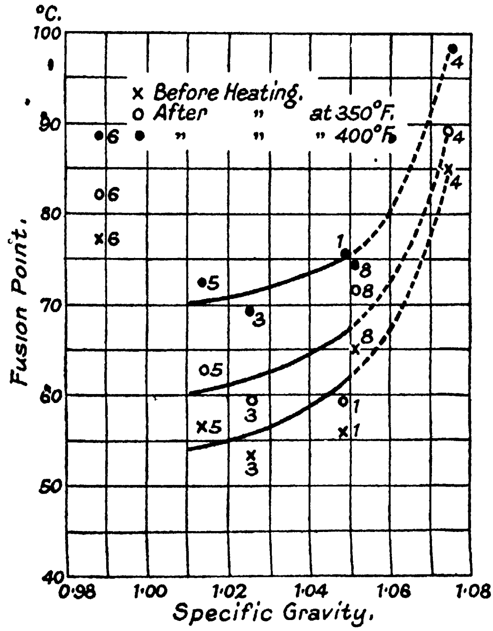


FIG. 15.—SPECIFIC GRAVITY AND FUSION-POINT.

relationship is doubtful. In the other curves they take their normal places.

The curves are self-explanatory, but the following comments may be of interest, both as regards the graphs and as giving certain broader generalisations.

1. *Specific Gravity and Fusion-Point* (Fig. 15).—A direct law would have been expected here, but a curved connection is the actual one when No. 4 is included.

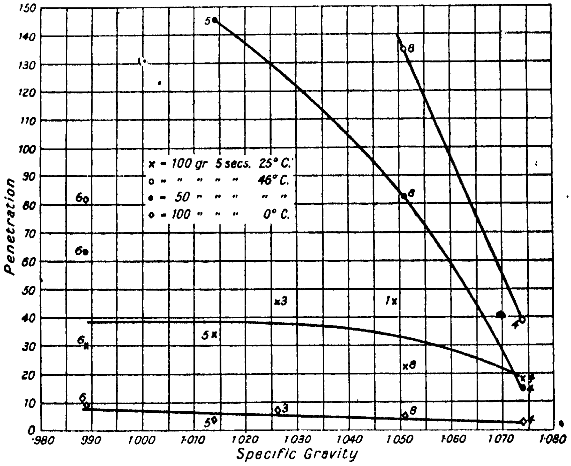


FIG. 16.—SPECIFIC GRAVITY AND PENETRATION.

2. *Specific Gravity and Penetration* (Fig. 16).—This shows a series of fairly good curves.

3. *Specific Gravity and Viscosity* (Fig. 17).—These curves show the sequence always to be observed in connection with the viscosity determination.

4. *Specific Gravity and Insolubility in Petroleum Ether* (Fig. 18).—This type of curve is also found in Figs. 21 and 35. Even excluding Nos. 4 and 6, the shape is not immediately to be interpreted.

5. *Fusion-Point and Penetration* (Fig. 19).—This relation might have been anticipated, on account of both properties being separately and intimately connected with the degree to which the material has been distilled or treated.

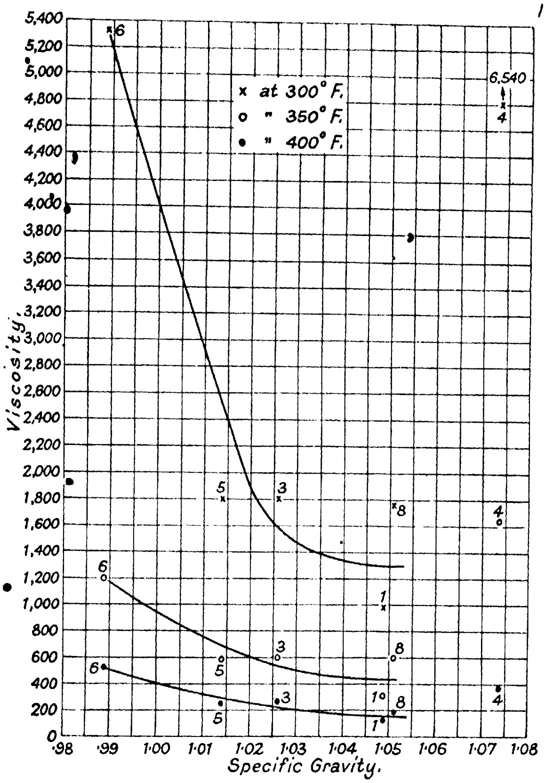


FIG. 17.—SPECIFIC GRAVITY AND VISCOSITY.

In this case 4 and 6 are not exceptional in their position.

6. *Fusion-Point and Ductility* (Fig. 20).—As in all ductility curves, the points available are not numerous, on account of so many results being +100. There are, however, enough to show, without doubt, the shape of the curve.

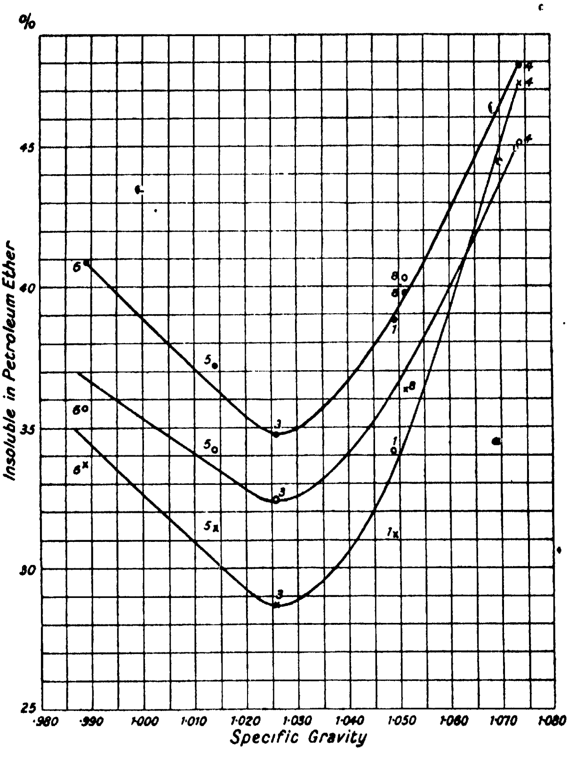


FIG. 18.—SPECIFIC GRAVITY AND INSOLUBILITY IN PETROLEUM ETHER.

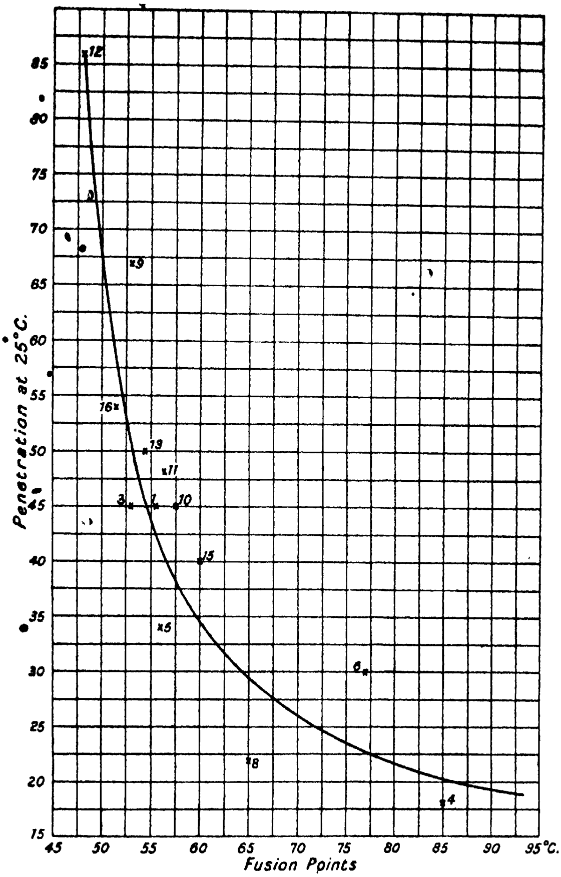


FIG. 19.—FUSION POINT AND PENETRATION AT 25° C.

7. *Fusion-Point and Viscosity at 300°, 350°, and 400° F.* (Fig. 21).—The 300° F. line alone causes much doubt as to the existence of any regularity, 4 and 6 giving direction in a cloud of points. But when the lower temperatures are also considered and the viscosities become more regular, a definite correlation is found to exist.

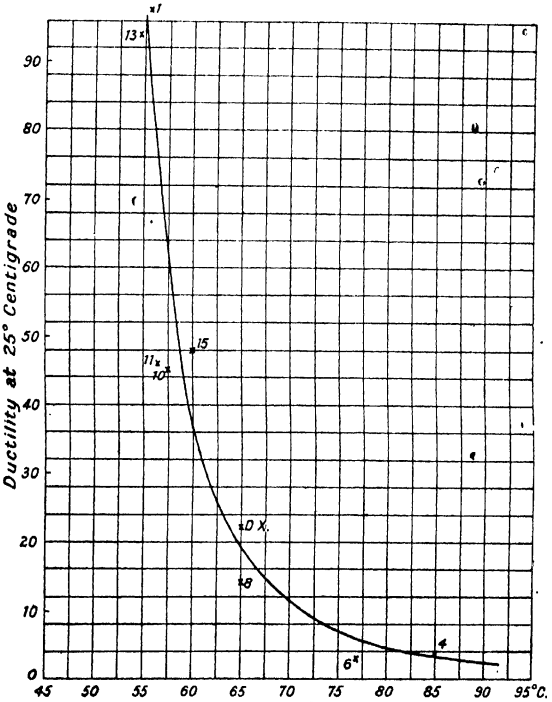


FIG. 20.—FUSION POINT AND DUCTILITY AT 25° C.

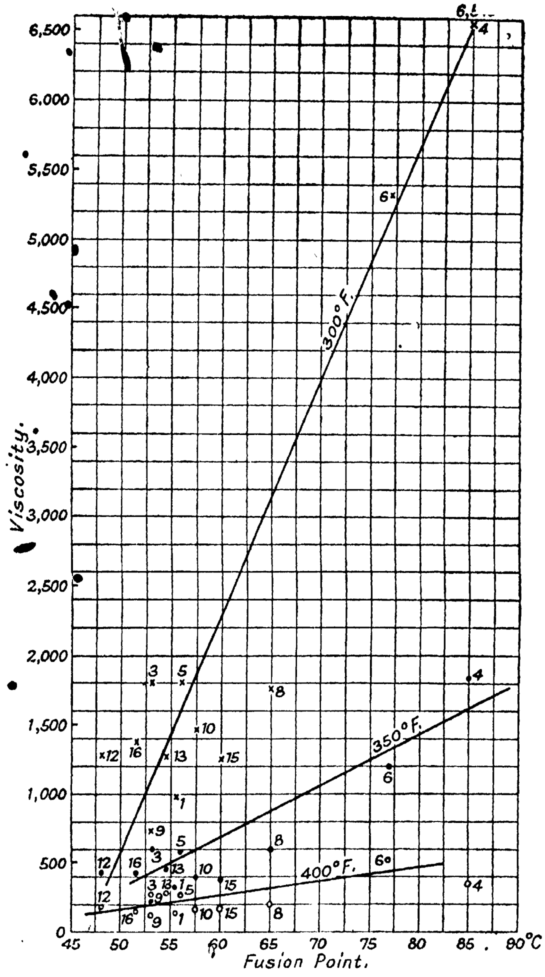


FIG. 21.—FUSION-POINT AND VISCOSITY.

I

Although 4 and 6 show exaggerated values, they take their places in the general law.

8. *Fusion-Point and Loss on Heating* (Fig. 22).—The exceptional behaviour of 4 and 6 is remarkable: they are out of the general scheme, yet fairly symmetrically placed to it.

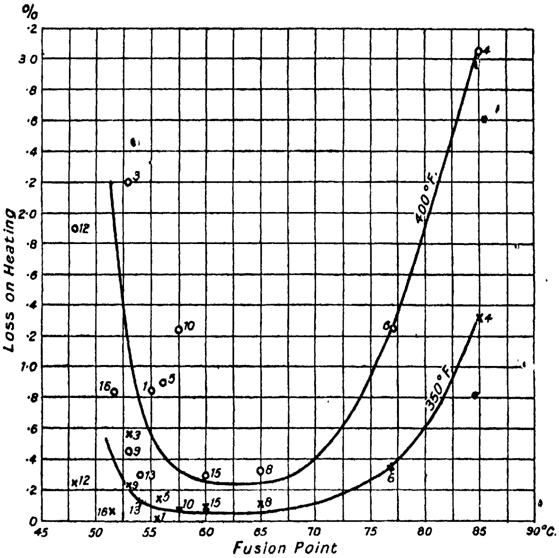


FIG. 22.—FUSION-POINT AND LOSS ON HEATING.

Their positions might be interpreted as indicating either that blowing has been carried out at a low temperature and under such conditions that the lighter oils have not been removed; or, more likely, that the chemical changes associated with a rise in fusion-point are accompanied by others leading to an approximately equal facility in disengagement of vapours due to decomposition.

9. *Fusion-Point and Insolubility in Petroleum Ether* (Fig. 23).—The line joining all points but two leaves no doubt that a general simple proportionality exists.

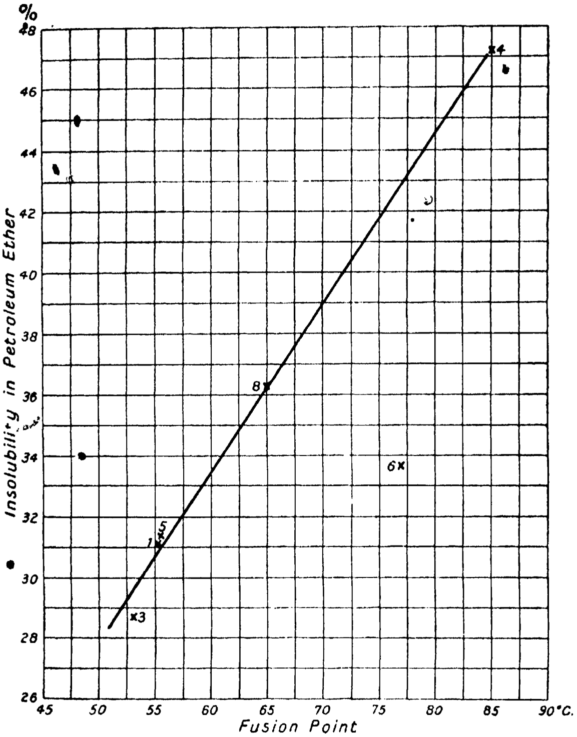


FIG. 23.—FUSION-POINT AND INSOLUBILITY IN PETROLEUM ETHER.

10. *Fusion-Point and Fixed Carbon* (Fig. 24).—Although so few points are available and one (No. 6) is exceptional, there is a regularity that cannot be ignored.

11. *Penetration and Ductility*, (*a*) at 0° C.; (*b*) at 25° C. (Fig. 25).

(*a*) The few figures available for comparison give no indication of regularity.

(*b*) (Fig. 25) This is of considerable interest, in that it is obviously demonstrated how successive heating causes increased dissemination of the points and a change in their relative positions: before heating these are fairly regular; after heating at 350° F., they are more scattered; whilst the points associated with heating at 400° F. cannot be connected even approximately by a curve.

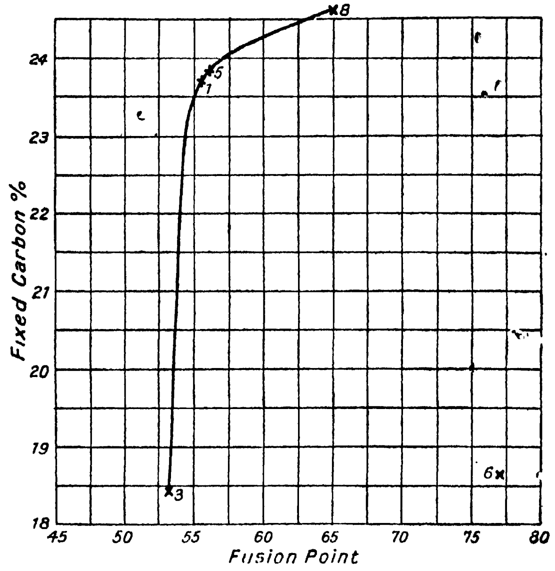


Fig. 24.—Fusion-Point and Fixed Carbon.

The significance of this is in the proof that increasing

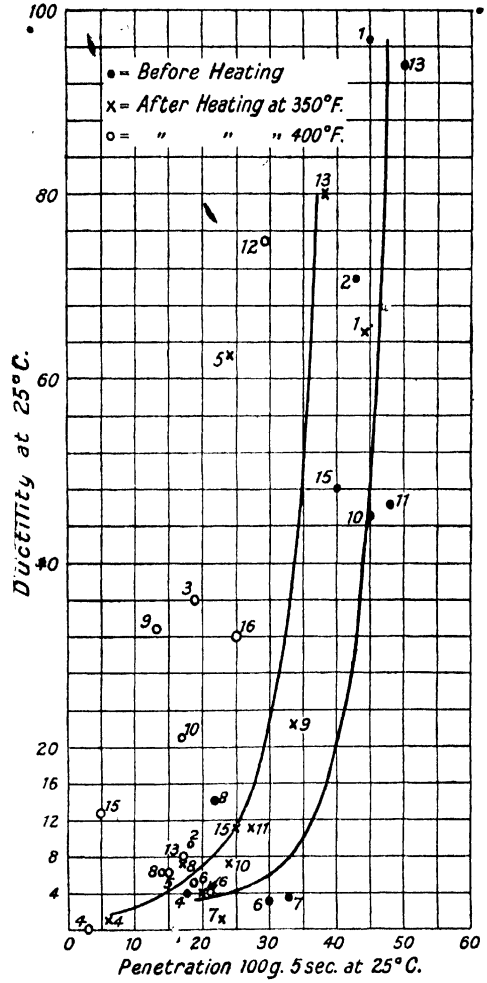


Fig. 25.—Penetration and Ductility.

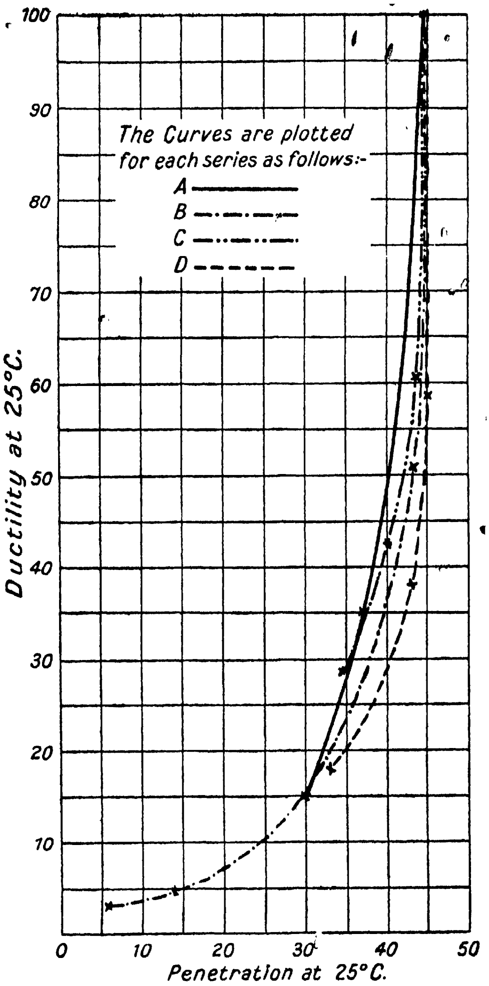


FIG. 26.—PENETRATION AND DUCTILITY.

heating upsets the fundamental characteristics of the samples more and more.

As these two properties are the most commonly tested and referred to, it is valuable to examine them more closely. The same kind of relationship as has already been found is apparent when one sample is heated under various conditions, such as is indicated in Table XX.

TABLE XX.

RELATION OF PENETRATION AND DUCTILITY: EFFECT OF HEAT.

Series.	*Temperature (Degrees C.).*	*Time of Heating in Hours.*	*Time Taken to Reach Temperature in Hours.*	*Penetration at 25° C.*	*Ductility, 25° C.*
A	100	—	—	47·1	87·0
	177	—	2	43·0	72·0
	177	6	—	37·6	34·0
	177	11	—	33·0	22·6
	177	15	—	30·5	15·8
B	288	5	—	13·8	4·5
	288	8	—	5·5	3·0
C	121	—	1·75	43·5	69·5
	121	5	—	43·0	55·1
	121	13	—	34·8	37·5
D Heated covered	177	—	2	44·6	77·3
	177	6	—	43·2	37·6
	177	12	—	33·0	17·8

These figures are shown in Fig. 26; and in both these series it is seen that for any change in nature of the bitumen, variation in ductility is much more rapid than that in penetration.

These curves undoubtedly substantiate the statement currently made that penetration and conductivity are inter-related so closely that knowledge of the one gives definite information as to the other. This is, however, another of those partially true statements that give so

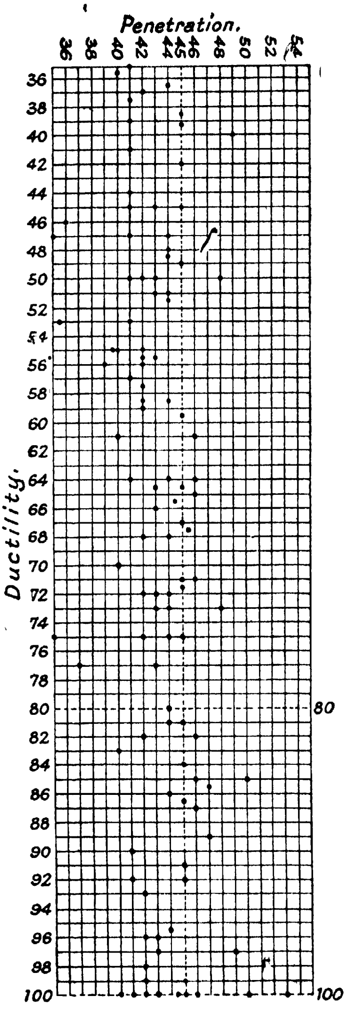


Fig. 27.—Penetration and Ductility "E" Grade Bitumen.

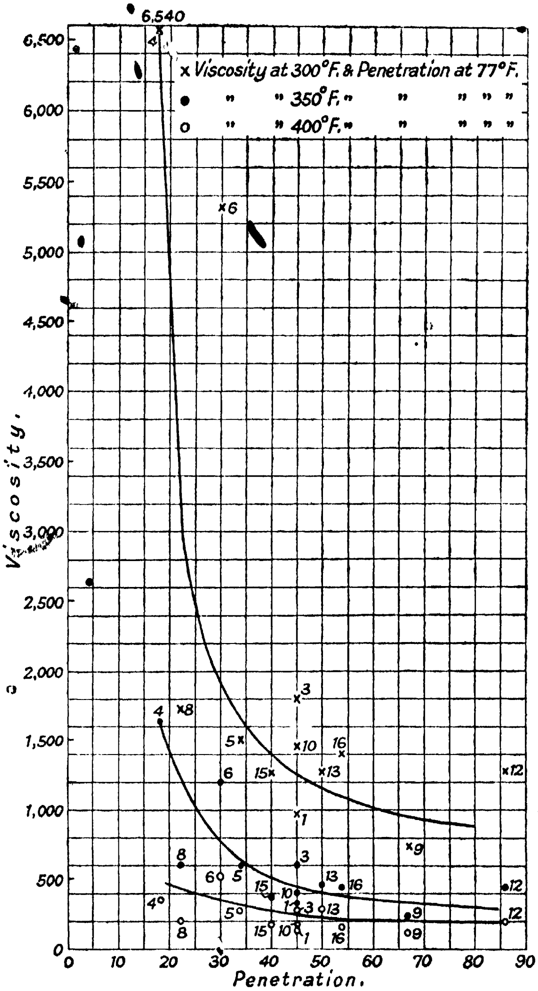


FIG. 28.—PENETRATION AND VISCOSITY.

much trouble. If careful account be kept of these two properties over a period of time, and they be plotted against one another as the above have been, no regularity whatever is to be found (see Fig. 27; see also [180]).

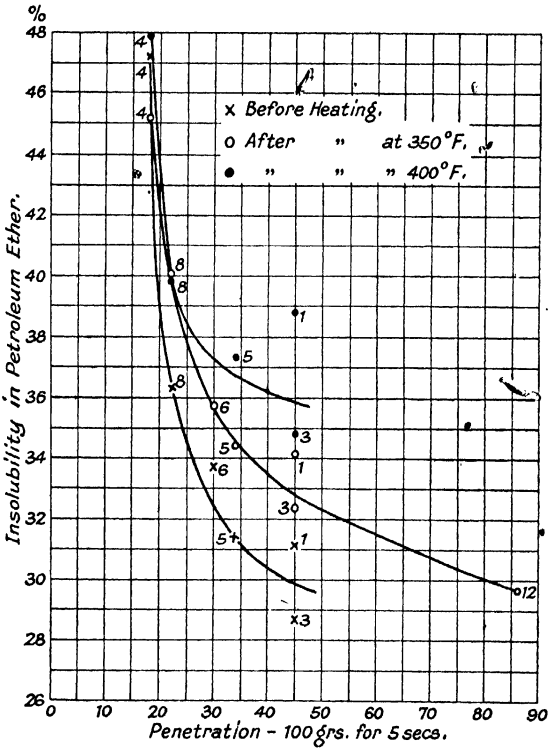


FIG. 29.—PENETRATION AND INSOLUBILITY IN PETROLEUM ETHER.

12. *Penetration and Viscosity* (Fig. 28).—These curves show the usual graduation of viscosity curves; No. 4 takes a normal position, but not No. 6.

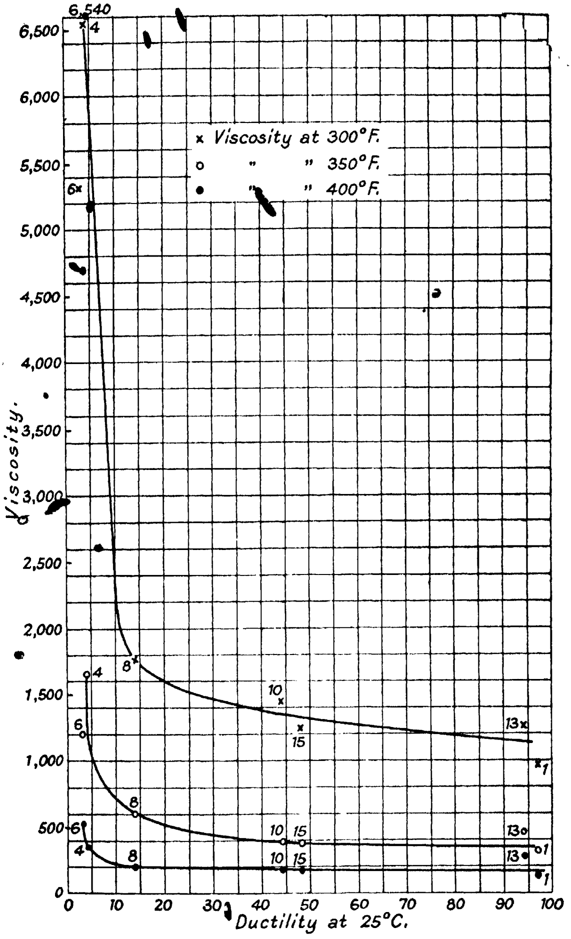


Fig. 30.—Ductility and Viscosity.

13. *Penetration and Insolubility in Petroleum Ether* (Fig. 29).—The regularity of these curves is undoubted, and calls for little comment.

14. *Ductility and Viscosity* (Fig. 30).—These curves follow the usual viscosity shape.

15. *Ductility and Insolubility in Petroleum Ether* (Fig. 31).—There are no comments to be made on this curve.

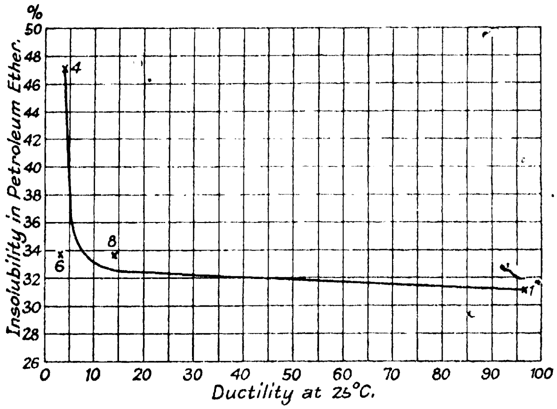


FIG. 31.—DUCTILITY AND INSOLUBILITY IN PETROLEUM ETHER.

16. *Viscosity and Loss on Heating* (Fig. 32).—Here have been compared the viscosity at the beginning of heating with the loss occurring during heating. This was necessitated by there not being sufficient material available for viscosity determinations after the period of heating.

The approximation to the average curves is not good, owing to both sets of determinations being somewhat irregular. They show, however, the remarkable effect of only 50° F. increase in temperature.

17. *Viscosity and Fixed Carbon* (Fig. 33).—The results are not very concordant, but are given as they indicate that there is a connection between the two properties.

18. *Loss on Heating and Flash-Point* (Fig. 34).—These curves show the expected connection, but not so consistently as might have been anticipated, No. 3 being widely separated from the curve.

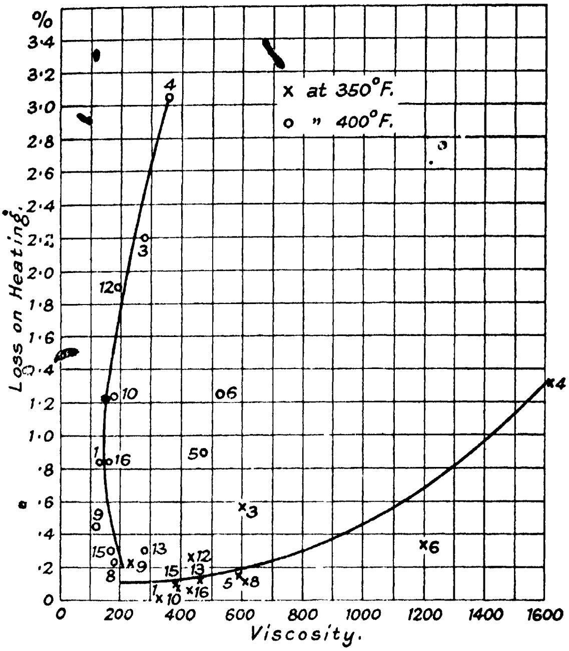


FIG. 32.—VISCOSITY AND LOSS ON HEATING.

19. *Loss on Heating and Fixed Carbon* (Fig. 35).—This relation is quite clear, 6 taking an exceptional position again.

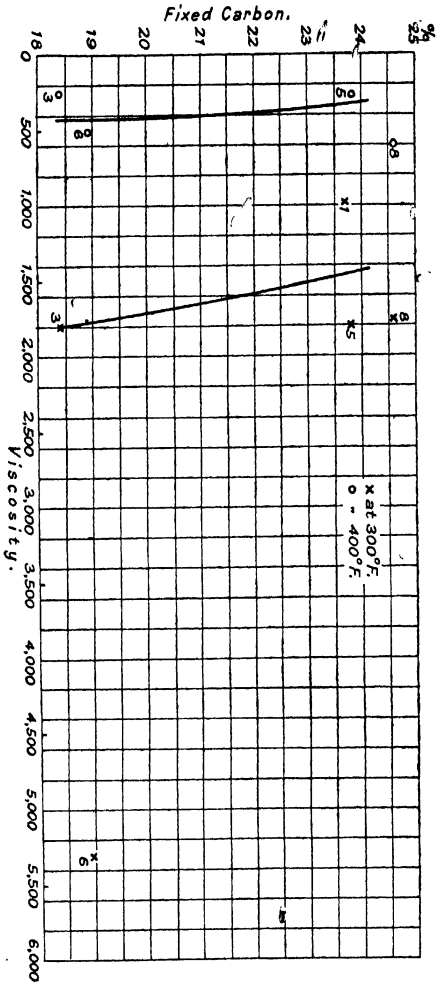


FIG. 33.—VISCOSITY AND FIXED CARBON.

20. *Flash-Point and Fixed Carbon* (Fig. 36).

21. *Fire-Point and Fixed Carbon* (Fig. 36).—It is doubtful whether this is a true and significant correlation; possibly not, as flash and fire points have to do with lighter oils, whilst fixed carbon is connected with the heavy residue; on the other hand, it might have been

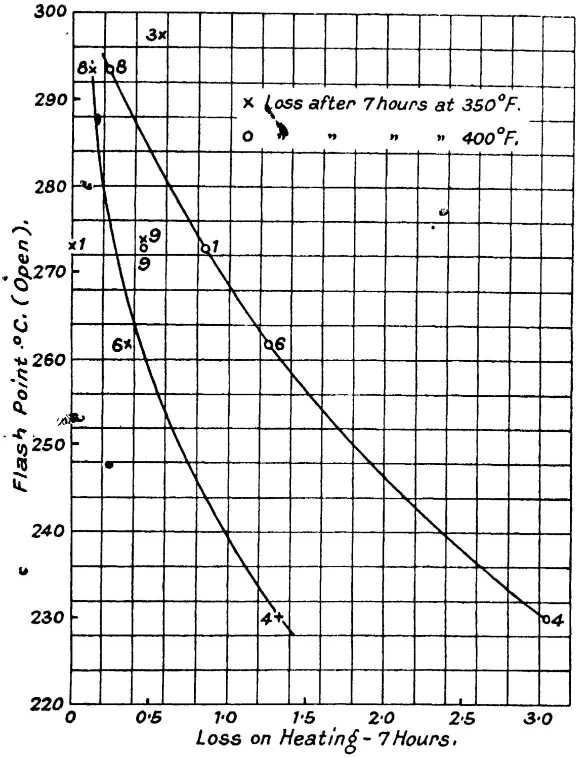


FIG. 34.—LOSS ON HEATING AND FLASH POINT (OPEN).

expected that some sort of reciprocal connection would have been shown. If the points Nos. 4 and 6 were omitted, as being exceptional, the remaining two would give a direction showing decrease of flash-point with

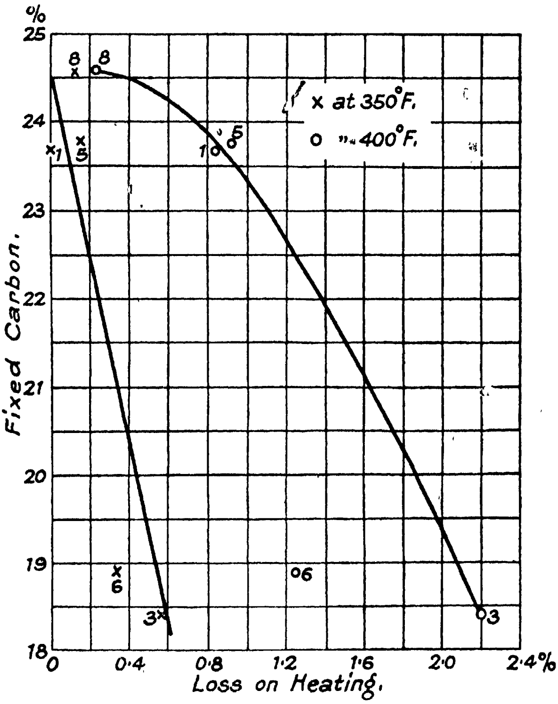


FIG. 35.—LOSS ON HEATING AND FIXED CARBON.

increase of unsaturated bodies. This would suggest increased facility of decomposition by heat.

22. *Insolubility in Petroleum Ether and Fixed Carbon* (Fig. 37).—There is an obvious connection between the two properties.

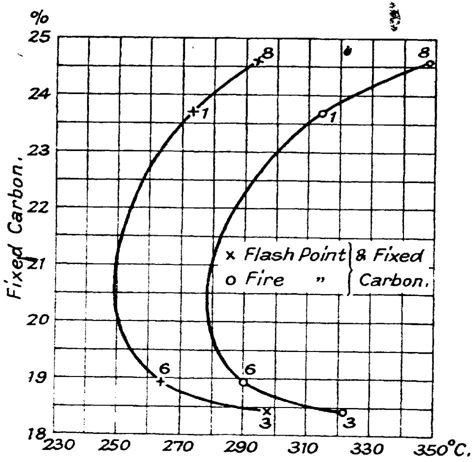


FIG. 36.—FLASH AND FIRE POINTS AND FIXED CARBON.

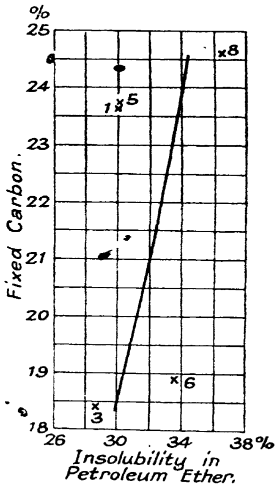


FIG. 37.—INSOLUBILITY IN PETROLEUM ETHER AND FIXED CARBON.

CONSIDERATIONS ON THE COMPARISON OF PROPERTIES AND SIGNIFICANCE OF THE CURVES.

Before going minutely into the matter, a general survey leads at once to the conclusions, first, that most of the curves are, as judged by the eye, parabolas or hyperbolas; and secondly, that there do exist a few straight-line laws between certain properties. This will be referred to later.

It is probably justifiable to judge the degree of importance of a property in indicating the nature of bitumen by the number of other properties with which it is in some definite relation. These figures are shown in Table XXI.

TABLE XXI.

SUMMARY OF CORRELATED PROPERTIES.—B.

Property.	*Number of Other Properties Connected.*
Fusion-point	7
Viscosity	6
Fixed carbon	5
Penetration	5
Insolubility in petroleum ether ..	5
Specific gravity	4
Ductility	
Loss on heating	
Flash-point	2
Fire-point	1

On the principle that "things that are equal" (or proportional) "to the same thing are equal" (or proportional) "to one another," it may be ultimately found that this statement will give completely a demonstration of the character of the bitumen.

It has been said that *fixed carbon* is a measure of the unsaturated constituents that are present (though doubt has been thrown on this statement (see also p. 135).

As a considerable proportion of the malthenes and probably all the asphaltenes consist of unsaturated substances (Clifford Richardson, p. 152), the fixed carbon determination rather widely overlaps in significance the solubility test; therefore, the latter is preferably to be taken as a measure of the quality of a particular bitumen. This may be as accurately and more clearly stated: that fixed carbon shows the extent of the deviation from the saturated hydrocarbons of paraffin petroleum.

Specific Gravity (Figs. 15, 16, 17, 18).—No straight lines—*i.e.*, no property is directly proportional to another.

With rising specific gravity, the fusion-point rises, the penetration falls as well as the viscosity; whilst the matter insoluble in petroleum ether shows anomalous results.

The fall of viscosity with rise of gravity is most remarkable, and if more were known of the chemical constitution of bitumen, should have considerable significance.

Fusion-Point (Figs. 15, 19, 20, 21, 22, 23, 24).—Some straight lines; otherwise similar.

The two measures of hardness, fusion-point and penetration, whilst supporting one another generally, are not proportional to one another. With increased hardness, ductility falls, viscosity rises, loss on heating diminishes, insolubility in petroleum ether rises, and content in unsaturated substances rises.

In all these relations the results are straightforward and coincide with previous experience.

Penetration (Figs. 16, 19, 25, 28, 29).—All similar curves, except one viscosity curve.

The exact significance of the penetration test is not clear. In itself it is a mixture of viscosity (flow due to the volume of the entering needle) and friction (steel against bitumen), but in general it is a measure of hardness. Probably it is on account of this two-fold indication that it is not exactly proportional to the fusion-point. Taking it to be, however, a measure of hardness, it is found to rise with lowered fusion-point, with rising ductility and lowered viscosity, as well as with diminished presence of asphaltenes.

As the variation of all these properties is in the direction demanded by change of hardness, penetration is a form of hardness test.

Ductility (Figs. 20, 25, 30, 31).—These are of the usual shape.

Whatever property this test illuminates—possibly a mixture of hardness and viscosity—the following associations are clear.

Ductility rises with decreased fusion-point, with increased penetration (but see p. 119), with decreased viscosity and diminished proportion of asphaltenes.

Except for there being no relationship between ductility and loss on heating and fixed carbon, ductility behaves in an exactly contrary fashion to fusion-point, showing that it is a sort of measure of softness, though, as experience shows, of a peculiar kind of softness.

Since it shows a regular relationship with insolubility in petroleum ether, and none with fixed carbon—*i.e.*, with asphaltenes but not with total unsaturated substances—a marked distinction is indicated between the behaviour of these two classes of substances.

Viscosity (Figs. 17, 21, 28, 30, 32, 33).—Viscosity and fusion-points are straight-line curves; with loss on heating the curves are peculiar; with fixed carbon they are straight lines. Otherwise they are probably hyperbolic, and show characteristic changes with temperature.

The physical significance of these curves is obscure, as the fundamental nature of viscosity and its dependence on chemical composition or physical connection in bitumens has not been worked out.

Loss on Heating (Figs. 22, 32, 34, 35).—These curves show no family relationship among themselves.

This is a measure of the degree that the material has been distilled—*i.e.*, hardened in the stills, or the degree that a too hard bitumen has been "cut back": the distinction between them being the quantity and boiling range of the distillate.

The curves show, for increasing loss, a higher fusion-point, and falling viscosity (much more rapid after heating at 400° F. than to 350° F.), a lower flash-point and lower fixed carbon.

These relationships for loss on heating are all associated with degree of distillation, hardness, and high boiling or flash points, natural to the materials.

Flash-Points Figs. 34 and 36 are unrelated; Fig. 36 is quite peculiar.

Rise of flash-point and fall of loss on heating are connected by an approximately straight-line law, whilst with the proportion of unsaturated substances (fixed carbon) the relation might also be a straight line if Nos. 4 and 6, so often exceptional, were excluded. Then, however, there would be too few points to judge from.

Fire-Point (Fig. 36).—This curve is quite peculiar.

See latter part of flash-point (above).

Insolubility in Petroleum Ether (Figs. 18, 23, 29, 31, 37).—Figs. 23 and 37 show straight lines.

This is accepted as being a measure of the proportion of asphaltenes present. This increases with increased hardness (rise of fusion-point and fall in penetration) and content in total unsaturated materials (by fixed carbon); it falls with ductility. This latter rather startling result may be explained as being fallacious in that it expresses a partial truth only; it shows the connection between ductility and asphaltenes only, whilst ductility results from all the constituents of bitumen; further, very few points are available for plotting, as so many are +100.

Fixed Carbon (Figs. 24, 33, 35, 36, 37).—Fig. 35 is peculiar, and the rest not far removed from straight lines.

This measure, as it may be, of the unsaturated compounds of all fusion and boiling points (since the quantity of evaporatable oils is, on the whole, extremely low) shows a relatively high number of traceable correlations, indicating its fundamental nature.

A rise in fixed carbon is accompanied by a rise in fusion-point, a lowering in viscosity, diminished loss on heating, and a sharp rise in insolubility in petroleum ether. This last is significant in the association of asphaltenes with unsaturated substances. With flash and fire points the association is doubtful. (For other similar comparisons see [190] and [191]; for comments, [192].)

CHEMICAL TESTS.

The chief of these tests, on which much work has been done, is (*a*) the separation of bituminous substances ("asphalt") from heavy oil; (*b*) the determination of fixed carbon; and (*c*) the detection of coal tar, which is the more usual of the additions that may be made to true bitumen.

(*a*) The *Separation of "Asphalt" from Heavy Oils* is a matter of precipitation by a liquid in which it is insoluble, and a number of such substances have been suggested.

For a time a light standard naphtha received much support. Filtration of the precipitated chloroform solution was to be assisted by bone charcoal on cotton-wool.[155] This same precipitant was employed in a micro-method applied to 0·2 to 0·5 gram of oil, which gave results as close as 0·1 to 0·2 per cent. to those obtained by Holde's method.[156]

In the laboratory the volumes of liquid used are of little importance, but in industry the relative quantity of light naphtha to oil was considered to be excessive, and this was reduced to a mixture of six times the quantity of light naphtha with one of crude amyl alcohol as fusel oil. Such a precipitate is separated the more quickly by centrifuging.[157, 158]

Ethyl and other acetates[159] and butanone[160] have also been suggested.

The ether-alcohol method is valuable and cannot be replaced by the use of light naphtha.[161] The settling of the precipitate which is formed can be accelerated by a few drops of an ether solution of ferric chloride and a few of alcoholic ammonia, whereby a flocculent precipitate is formed without disturbing the existing proportion of ether and alcohol already present.[49]

A long paper emphasising the uncertainty of the ether-alcohol method, the desirability of using ethyl and propyl acetate and the necessity of restricting the limits of composition of the standard naphtha even to using *n*-hexane,[162, 163] has been severely criticised by Holde. The use of this solvent has recently been further opposed,[164] on the ground that hexane gives much less asphaltene precipitate than does light naphtha. (See also [179, 181, 182].)

Finally, doubt has been thrown on the whole question of determining "asphaltic content" as being too susceptible to inaccuracies; and the recommendation has been made that it should be abandoned in favour of a physical method that is proportional to it.[165]

(*b*) *Fixed Carbon* is considered to be a measure of the degree of condensation of a particular class of hydrocarbon (C_nH_{2n+2} gives no free carbon), whether produced naturally or artificially. It is an indication of the severity of heat treatment that the material has undergone, ranging from small evidences to the presence of carbenes and free carbon.

Although the details of the estimation are carefully laid down, considerable variation may occur from differences in heating value of the gas and even of the condition of the crucible employed, and serious disturbances may occur from tendencies to frothing. Two samples tested in six laboratories gave variations of 6 and 9 per cent. As the fixed carbon figures are to be associated with the relative solubility of the sample and with the consistency tests, it is recommended that the latter should be substituted.[166, 167]

In the works, it is argued that the amount of coke finally remaining in the oil stills is a measure of the "hard and soft asphalts" in the oil.[168]

(*c*) *Identification of Coal Tar Derivatives in Bitumen.*—From early times tar products have been added to bitumen (p. 11), and only the *appearance* was then relied on to detect the admixture. To-day the addition, made for technical purposes, is to be ascertained, according to one investigator, by almost the same method of examination, where a careful series of trials have shown that a solution of 1 gram of the substance in 25 c.c. carbon disulphide, when allowed to evaporate spontaneously, leaves residues sufficiently characteristic for differentiation between natural bitumen, petroleum residues, tar from schist, stearine, etc., and mixtures.[169]

More usually chemical tests are applied, based either on the identification of a particular substance, such as phenol, or on a general reaction such as saponification.

The test of the *coloration of alcohol* which is given as a test for the presence of tar products has been found to fail in a case of an undoubted specimen of the natural substance.[170]

The earlier method of *identifying phenol* was to heat the suspected substance, catch the vapour on a glass rod, transfer to alkaline water, and to add diazobenzene chloride; if phenol were present, a red colour resulted.

This was improved by Graefe, who acted on the sample with sodium hydroxide and added diazobenzene chloride to the filtrate; a yellow colour indicated no phenol; a red to red-brown colour showed the presence of a little phenol; and a precipitate, of much phenol.

Certain anomalies and intermediate colorations led Loebell to extract the bitumen, after mixture with sand, with colourless acetone. A colourless or pale yellow extract indicated absence of phenol, but if the liquid was strongly coloured the diazobenzene chloride test was applied.[171] A development of this procedure has led to the following identifications:

Brown, non-fluorescent extract, negative diazo-reaction: natural bitumen.

Brown to yellow extract, strong yellow-green fluorescence, negative diazo-reaction: petroleum residues.

Yellow extract, dark green fluorescence, positive diazo-reaction: coal or lignite tar products.[172]

The problem has been attacked by an interesting application of the *formolite reaction.* After eight hours under a reflux condenser with 50 parts phenol and 30 parts of 40 per cent. formol, tar pitches, oil residues, etc., give products soluble in the reacting liquid, whilst those from bitumen, gilsonite, albertite, etc., are insoluble.[173] This type of reaction should be very carefully studied before full reliance be placed upon it. (See [199].)

The *action of sulphuric acid* can be made to be of significance, as the products of distillation of coal tar are mainly soluble in the acid and those from bitumen are, to a considerable degree, insoluble. For mixtures in which the proportion of bitumen is less than 20 per cent., the method has been refined by acting on the sample itself with sulphuric acid, filtering through bone charcoal, extracting this with light naphtha, and separating the free sulphur from the residue by acetone. The residue from pitch is 0·1 to 0·2 per cent.; that from bitumen is 1 to 35·7 per cent.[174] Evidently any quantitative interpretation from the results must be based on intimate knowledge of the properties of the constituents of the mixture.

The acid value and the saponification figure[175, 176] have been made use of, natural substances giving the higher figures in both cases.

The presence of sulphur is of some assistance. The estimation, by burning in oxygen (which is a safer and more accurate procedure than the Carius method), is not of much help[175]; but the generation of sulphuretted hydrogen by heat has greater significance. Considering that petroleum residues have been prepared by heat, these should cause a minimum blackening of lead acetate paper on being heated as compared with the naturally occcurring bitumen, and this actually occurs. The asphaltites, however, give no reaction.[176]

The distinction between coal and certain naturally occurring "asphalts" in the field is rather outside the scope of this book, yet one reference might be included on account of certain intrinsic and reflecting interest. The observations were made particularly in connection with certain Peruvian deposits, which had the closest similarity in appearance with local coal beds. The asphalts were found, however, associated with calcareous mesozoic deposits that had been, and were still, petroliferous; the coal occurred in deposits of other ages, and associated with non-petroliferous detritus. The hydrocarbon deposits were subsequent to the surrounding rocks, the coal contemporaneous. The hydrocarbons contained vanadium, and the reddish and blue salts were to be identified, especially in association with surface water; the coal contained no vanadium.[177]

CHAPTER VI

CONCLUDING REMARKS

It is a well-known quip that "the technical chemist does things and the scientific chemist tells him how he has done them"—it is always the technical chemist who repeats this.

In the case of, say, soap manufacture, this order of events may have been justified, otherwise we might have had to wait for the explanation of detergent action before we could make use of its results. In the present case it is also true that valuable uses have been made of bituminous substances before their composition has been fully elucidated and whilst methods of ascertaining their nature are still mainly empirical and arbitrary.

These uses may be broadly summarised into sections: (*a*) general protection of objects by painting; (*b*) waterproofing, by means of roofing felt, damp-courses, and the like; (*c*) electric insulation; (*d*) miscellaneous uses, such as rubber substitute, axle grease, and so on; (*e*) moulded objects; (*f*) roofing and flooring mastic, and road-making mixtures whether employed in the form of asphalt macadam, mastic, or grout.

In all these modes of employment, and in its preparation for use, the material is necessarily heated at least once; and there can be no doubt that those changes that occur when this is at all over-done, which have been noted and emphasised in an earlier chapter, are as detrimental in other cases as in, for example, road-making. The obvious inference is to do without heat—to manufacture cold. This, at the present time, is impossible and even fantastic; but if it ever is achieved a great step will have been taken in the development of bitumen technology, and greater regularity of the quality of the products will result. Stabilisation of the material from slow change, whether under the influence of weathering or not, is another urgent problem to be solved.

These are but the more immediately obvious examples on the technical side of the large amount of work to be done in the perfection of the treatment of the material. On the scientific side, the very obvious gaps in knowledge that are so clearly to be noticed in the proceeding pages show the direction in which investigation is required.

The one way in which this may be achieved is for the producers and users of bituminous products not to rest too content with their methods, their processes, treatments and handling—let there be healthy, constructive discontent.

APPENDIX A

THE NOMENCLATURE OF BITUMINOUS (ASPHALTIC) SUBSTANCES

THE terms employed have for long been varied, contradictory, and "out of joint"; and many have been the attempts to put an end to the confusion, with the result, on the whole, of increasing it. At last a final attempt—final, at any rate, for this country—is to be made to "set it right."

The matter would not be difficult to settle if it were possible to start from the beginning; but, in order to reach the most acceptable scheme of nomenclature, it is necessary to take into consideration the practice of other nations, the custom of the trade, the habit of the public; whilst at the same time leaving open the way towards the achievement of the ultimate haven of finality—an international understanding on the matter—as a culmination of separate national effort.

The chief controversy will certainly be concerned with the words "bitumen" and "asphalt," because these are most usually taken either to be almost synonymous, or to be sharply contrasted; and also, because they are the two words most frequently in the lay mouth when talking of such materials and their uses.

The word "bitumen" is derived from *pix tumens* (swelling pitch), and was originally connected with the substantially mineral-free naturally occurring petroleum product, soluble in carbon disulphide. Later, the word was made to cover bitumen-substitutes manufactured from natural oil. Consciously or otherwise, this has been followed closely by the British scheme of nomenclature of 1916.[19] Later still, it included coal and wood tar derivatives, in spite of the fact that these are not totally soluble in carbon disulphide or benzene;

and to-day it can include natural hydrocarbons and distillation residues of oils, coal, fats, peat, schist, etc., of varied solubilities."

This extension of meaning of the word "bitumen" has taken place in Germany and America, and therefore claims very serious attention, but it must be carefully considered, firstly, how far a word is of value when it is made to cover an increasingly various miscellany of substances, and how far it is justifiable for coal tar products to be called "bitumen," and, conversely, for certain undoubted petroleum products to be called "tars," as it can hardly be doubted that such comprehensive significance was adopted for purely commercial purposes, even though their properties, except the superficial ones, are so very different from those of what was originally, and is usually, known as bitumen.

"Asphalt" is a word of obscure origin, and works of reference will not commit themselves farther than to state that *asphaltos* is not a Greek word, but an Eastern word of Greek form.

These two words "bitumen" and "asphalt" appear to be the only important ones of long standing, all the rest being modern inventions to satisfy increasing requirements.

For the sake of convenience of consideration these various terms, with their definitions, have been grouped together in alphabetical order, and in order, also, of date of publication, so that the development of thought can be traced; and as an introduction to this a little may be said on the papers, articles and books in which they and their groupings have been made public.

In 1906, in Germany, "Problem 34: Fixing a Uniform Definition and Nomenclature for Bitumen," was reported upon by a committee presided over by the late Professor G. Lunge, to the International Association for

Testing Materials, which held a Congress at Brussels. This report was severely criticised by Peckham (1907)[13] with, apparently, considerable justification. Peckham himself advanced a scheme with which that of Abraham showed a close family resemblance.

Clifford Richardson (1908)[14] may be considered to be the "father of the modern asphalt pavement," and his views on bitumen and its relationships are the prototype of many that followed. That he was fully alive to the difficulty of classification is shown in his remarks as to the empiricism of his and others' schemes, and that "a final conclusion . . . can only be arrived at after years of investigation of the subject."

Holde and Marcusson in 1912 produced their "family tree" in a publication of the Deutsche Verband für die Materialprüfungen der Technique. This I have not been able to study, but it is doubtless the same as that of Holde and Marcusson, in the Proceedings of the Sixth Congress of the International Association for Testing Materials, 1912,[15] and of Holde, published in *Petroleum* in the same year.[16]

In the following year, 1913, in America, Abraham[17] put forward his ideas, which show a considerable general likeness to the German schemes, and will be seen to be of considerable complexity. (It should be noted that in his original paper Abraham gives detailed reasons and comments on every significant word used in his definitions.)

In the same year, 1913, Engler[18] published a paper on bitumen which included certain definitions based on important chemical observations and reasoning. His scheme does not help very much, but it has been included for the sake of the originality of its grouping as compared with the rest.

In 1916 appeared a Report by the British Engineering Standards Committee,[19] embodying their views as to the most practical meaning of the words "bitumen" and "asphalt." Dealing with the matter from the road engineers' point of view, they considered it desirable to differentiate sharply between the derivatives of coal tar and paraffin oil and asphaltic oil residues on the one hand, and native bituminous substances on the other—and this in spite of their anxiety to correspond, if possible, with American practice. Good as these definitions practically are, there seems, however, to be a lack of logic that it would be desirable to rectify. There is almost a contradiction in the statements that bitumen occurring in nature is soluble in carbon disulphide, but that native bitumen is not so soluble. Also, that a native bitumen containing mineral matter is a bitumen, but that if admixed mineral matter is finely graded it is an asphalt for road purposes.

In 1918 the American Association for Testing Material[20] published a series of definitions, of which those of interest to us have been included in the collection that follows.

In 1918, also, Abraham,[21] in the book particularly associated with his name, published another series of definitions, of appreciable difference from those of 1913. The only comment of importance to be made is on the great similarity between the meanings ascribed to "bitumen" and "asphalt," whereby the opportunity for a useful and significant contrast is lost.

Later, in 1922, the views of Professor Mrazek,[22] evidently written in French, were published in a somewhat unfortunate translation; but they do not help the matter forward very much.

In 1920[23] and 1922[14] Hackford put forward his scheme of nomenclature for the different types of what are usually known as bitumens and asphaltites. Its construction is very good, in that it is based on intimate chemical knowledge of the substances, and the whole scheme is clear and short. All classes of solid natural bitumens are covered by the term *petrolite*, those soluble in carbon disulphide are *asphaltites*, and those insoluble in the solvent are *kerites*, the termination "ite" emphasising the natural occurrence of the substance. Hackford also adopts a very wide meaning to the term "bitumen."

Finally, in 1923 appeared a Report by Le Gavrian and Feret[25] to the Commission Permanente de Standardisation, which aimed at following the clearness of the British scheme, whilst keeping open the way for linking up ultimately with the American. No distinction has been made between the natural and the artificial products, as it was considered that constitution alone mattered.

DEFINITIONS

(*In alphabetical order and in order of date of publication*).

The attention paid here to pyrobitumen, coal and wood, tar and pitch, wax and resins, is incomplete and only enough to indicate the fundamental difference from petroleum and its products which is the prime consideration of this book.

ASPHALT.

1. *Richardson*,[14] 1908.—Asphalt is a bitumen, found in nature, originating in certain types of petroleum, generally softening about 100° C., consisting of saturated and unsaturated hydrocarbons and their derivatives, partly soluble in petroleum naphtha, and reciprocally soluble in carbon disulphide and in carbon tetrachloride.

2. *Abraham*,[17] 1913.—A dark coloured and more or less viscous to solid hydrocarbon complex, including (*a*) the easily fusible bitumens often associated with a mineral matrix, not having a "waxy" lustre or unctuous

feel; (*b*) fusible residua obtained from the distillation, oxidation, sulphurisation, etc., of bitumens.

3. *Richardson,*[26] 1916 (Summarised). — Residual pitches from asphaltic petroleums. Includes all forms of bitumen, native and manufactured, which are employed in pavement and road construction, as well as gilsonite and grahamite, " which, in a strict sense, are sharply differentiated from asphalt."

(Quoting Northrup in "Mineralogical Research of the United States," 1915, part. ii., p. 135).—" In the broad sense natural asphalt may be used to denote all types of naturally occurring asphaltic substances that are employed in the arts and industries," and include maltha, grahamite, gilsonite, elaterite; bitumen-impregnated sandstone, limestone and shale; ozokerite. " Manufactured asphalt " includes residues from distillation of asphaltic and semi-asphaltic petroleum.

4. *British Committee,*[19] 1916. *Definition of Asphalt.*—Asphalt is a road material consisting of a mixture of bitumen and finely graded mineral matter. The mineral matter may range from an impalpable powder up to material of such a size as will pass through a sieve having square holes of ¼ inch side.

Definition of Native or Rock Asphalt.

Native or rock asphalt is a rock which has been impregnated by nature with bitumen.

5. *A.S.T.M.,*[20] 1918. — Solid or semi-solid native bitumens, solid or semi-solid bitumens obtained by refining petroleum, or solid or semi-solid bitumens which are combinations of the bitumens mentioned with petroleum or derivatives thereof, which melt upon the application of heat, and which consist of a mixture

of hydrocarbons and their derivatives of complex structure, largely cyclic and bridge compounds.

Artificial Asphalt.—Recommended that the use of the term be discontinued.

6. *Abraham,*[21] 1918.—A term applied to a species of bitumen, also to certain pyrogenous substances of *dark colour,* variable hardness, comparatively non-volatile; composed of hydrocarbons, substantially free from oxygenated bodies; containing relatively little or no crystallisable paraffins; sometimes associated with mineral matter; the non-mineral constituents being *fusible,* and largely soluble in carbon disulphide, and whose distillate fractionated between 300° and 350° C. yields *considerable sulphonation residue.*

Note.—This definition is applied to native asphalts and pyrogenous asphalts. Native asphalts include asphalts occurring naturally in a pure of (*sic*) fairly pure state, also asphalts associated naturally with a substantial proportion of mineral matter. Pyrogenous asphalts include residues obtained from the distillation, blowing, etc., of petroleum . . . also from the pyrogenous treatment of wurtzilite—*e.g.*, wurtzilite asphalt. (See " Wax," *Abraham,* 1918.[21])

7. *Mrazek,*[22] 1922.—Asphalt is a more or less oxidised solid bitumen, of a dark colour and with a degree of plasticity. In its composition it is a mixture of saturated and non-saturated hydrocarbons, with the addition of hydrocarbonic compounds, embodying oxygen, nitrogen, and sulphur. The sulphur is also in part in a colloidal state, similar to that of sulphur in vulcanised rubber.

8. *Le Gavrian and Feret,*[25] 1913.—Naturally occurring rocks, containing less than 20 per cent. pure bitumen and soluble in carbon disulphide.

ASPHALTENES.*

1. *Richardson*,[14] 1908.—Hydrocarbons and derivatives soluble in carbon disulphide and in carbon tetrachloride.

2. *A.S.T.M.*,[20] 1918.—The components of the bitumen in petroleum, petroleum products, malthas, asphalt cements and solid native bitumens, which are soluble in carbon disulphide, but insoluble in paraffin naphthas.

3. *Hackford*,[23] 1920.—Those portions of bitumen that are insoluble in ether or ether alcohol, but are soluble in carbon disulphide.

ASPHALTITE.†

1. *Abraham*,[17] 1913.—A dark coloured, solid, difficultly fusible, naturally occurring hydrocarbon complex, insoluble in water, but more or less completely soluble in carbon disulphide, benzole, etc. (Examples of properties given.)

2. See "Pitches," 3.

3. *Engler*,[27] 1912.—Asphalt is the material resulting from the oxidation and polymerisation of petroleum or one of the stages of conversion.

4. *Abraham*,[21] 1918.—A species of bitumen, including dark coloured, comparatively hard and non-volatile solids, composed of hydrocarbons substantially free from oxygenated bodies and crystallisable paraffins; sometimes associated with mineral matter, the non-mineral constituents being *difficultly fusible*, and largely soluble in carbon disulphide; and whose distillate fractionated between 300° and 350° C. yields *considerable sulphonation residue*.

NOTE.—This definition includes gilsonite, glance pitch and grahamite.

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* Term introduced by Clifford Richardson.

† Term introduced by Eldridge, 22nd Annual Report, U.S. Geologica Survey, 1901.

5. *Hackford*,[23] 1920.—Those solid or semi-solid natural bitumens that are composed for the most part of asphaltenes or diasphaltenes.

6. *Marcusson*,[28] 1921.—This term covers gilsonite, grahamite and manjak (as in Abraham, 1918); also albertite and wurtzilite.

Hackford,[24] 1922.—See Scheme.

BITUMEN.

1. *Richardson*,[14] 1908.—Bitumens; for scope, see Table.

2. *Abraham*,[17] 1913.—A naturally occurring hydrocarbon complex often associated with a mineral matrix, insoluble in water, but largely soluble in carbon disulphide, benzole, etc. Its colour and hardness are variable.

3. *Engler*,[27] 1912.—Bitumen covers all stages of the conversion from sapropel wax, montan wax, and the like, to petroleum.

4. *British Committee*,[19] 1916. *Definition of Bitumen.*—Bitumen is a generic term for a group of hydrocarbon products soluble in carbon disulphide, which either occur in nature or are obtained by the evaporation of asphaltic oils. The term shall not include residues from paraffin oils or coal tar products.

NOTE.—Commercial materials may be described as bitumen if they contain not less than 98 per cent. of pure bitumen as defined above.

Definition of Native Bitumen.

Native bitumen is bitumen found in nature, carrying in suspension a variable proportion of mineral matter.

The term " native bitumen " shall not be applied to the residuals from the distillation of asphaltic oils.

5. *A.S.T.M.*,[20] 1918.—Mixtures of native or pyrogenous hydrocarbons and their non-metallic derivatives, which may be gases, liquids, viscous liquids, or solids, and which are soluble in carbon disulphide.

6. *Abraham*,[21] 1918.—A generic term applied to native substances of variable colour, hardness and volatility; composed of hydrocarbons substantially free from oxygenated bodies; sometimes associated with mineral matter, the non-mineral constituents being *fusible* and largely *soluble* in carbon disulphide; and whose distillate fractionated between 300° and 350° C. yields *considerable sulphonation residue.*

NOTE.—This definition includes petroleums, native asphalts, native mineral waxes and asphaltites.

FOOTNOTE.—The interpretation of the term bitumen as employed in this treatise is entirely dissociated from the idea of *solubility* (in certain solvents for hydrocarbons), and has no connection whatsoever with the inappropriate phrase "total bitumen," used in many contemporary textbooks to designate the amount soluble in carbon disulphide, and which perhaps is largely responsible for the existing confusion in the terminology.

7. *Hackford*,[23] 1920.—A naturally occurring organic substance, gaseous, liquid, or solid, consisting of hydrocarbons and the oxy- and thio-derivatives of the same, or of a mixture of all three.

8. *Le Gavrian and Feret*,[25] 1923.—A group of naturally occurring hydrocarbons, solid, semi-solid, or liquid, soluble in carbon disulphide, poor in volatile constituents, containing sulphur, oxygen and nitrogen compounds, with or without admixture of water, mineral substances, and organic detritus. They should have agglomerating or adhesive properties.

They may be divided:

Crude bitumen.

Epuré, by fusion.

Refined, by additions to modify properties, the bitumen remaining in dominant proportion. Nature and provenance always to be stated.

BITUMINOUS SUBSTANCES.

1. *Abraham*,[17] 1913.—A term applied to (*a*) substances containing bitumens or pyrobitumens; (*b*) substances resembling either the viscous or solid bitumens or pyrobitumens in their solubility and physical properties—*i.e.*, having an amorphous structure and darker colour in mass.

2. *British Committee*,[19] 1916. *Prefixes denoting Source of Origin.*—The Committee recommend that for convenience of identification prefixes denoting geographically the source of origin should be attached to each of the four terms defined above.

3. *Abraham*,[21] 1918.—A definition, substantially the same as No. 1, covers bitumens, pyrobitumens, pyrogenous distillates (pyrogenous waxes and tars) and pyrogenous residues (pitches and pyrogenous asphalts).

4. *Mrazek*,[22] 1922.—A characteristic feature of all natural " free bitumena " is their total, or almost total, solubility in organic solvents—light hydrocarbons, carbon tetrachloride, carbon disulphide, chloroform, ether, alcohol, turpentine, benzole, etc.

CARBENES.

1. *Richardson*,[14] 1908.—Hydrocarbons and their derivatives soluble in carbon disulphide, but insoluble in carbon tetrachloride.

2. *A.S.T.M.*,[20] 1918.—The components of the bitumen in petroleum, petroleum products, malthas, asphalt cements and solid native bitumens, which are soluble in carbon disulphide, but insoluble in carbon tetrachloride.

CARBOID.

Marcusson,[29] 1918. (Summary.)—That portion of asphaltites that is insoluble in organic liquids.

DIASPHALTENES ("SOFT ASPHALT.")

Hackford,[23] 1920 (Summarised).—Diasphaltenes consist of that portion of bitumen soluble in ether or carbon disulphide, but insoluble in a mixture of equal parts of ether and alcohol.

KERITE.

Hackford,[23] 1920.—Natural solid bitumen, composed for the most part of kerotenes (and insoluble in carbon disulphide).

KEROLES.

Hackford,[23] 1920.—Those portions of kerotenes that are insoluble in chloroform, but soluble in pyridine.

KEROLS.

Hackford,[23] 1920.—Those portions of kerotenes that are soluble in chloroform as well as in pyridine.

KEROTENES.

Hackford,[23] 1920.—Those portions of bitumens insoluble in carbon disulphide.

MALTHA.

1. *Richardson*,[14] 1908.—Viscous, naturally occurring bitumens approximating in consistency to artificial residuums.

2. *Abraham*,[17] 1913.—A dark coloured and viscous, naturally occurring hydrocarbon complex, insoluble in

water, but completely soluble in carbon disulphide, benzole, etc. (See also "Tar.")

3. *Abraham*,[21] 1918.—"Omitted for the sake of brevity."

4. *Le Gavrian and Feret*,[25] 1923.—Natural viscous bitumen, between petroleum and bitumen, rarely suitable for mixing with bituminous products for constructions. Fairly rich in hydrocarbons, volatile at 160°.

MALTHENES.

Richardson,[14] 1908.—Naphtha-soluble bitumen (associated with the naphtha-insoluble asphaltenes).

MINERAL ROSIN.

Abraham,[17] 1913.—A term applied to solid bitumen (*vide* "Bitumen").

PETROLITE.

Hackford,[24] 1922.—The term "petrolite" covers all classes of solid bitumen.

PITCH.

1. *Abraham*,[17] 1913.—A dark coloured, fusible, and more or less viscous to solid bituminous and resinous substance, insoluble in water, but more or less completely soluble in carbon disulphide, benzole, etc. Its composition and origin are variable.

(*a*) Natural: Resulting from a slow natural process of metamorphosis known as "mineral pitches" or natural asphalts—*e.g.*, Trinidad pitch, glance pitch, gilsonite, etc.

(*b*) Artificial: (1) Residues from the distillation, oxidation, etc., of mineral oils—*e.g.*, petroleum pitch, blown petroleum, asphalt, sludge pitch, Dubb's asphalt, etc.

(2) Residues from the distillation of tars (examples).

(3) Residues from the distillation of fusible organic substances, the process having terminated before the actual formation of coke—*e.g.*, resin pitch, stearin pitch, (fatty acid pitches), etc.

(4) Artificial mixtures complying with the above general definition of the term " pitch " regardless of their origin or composition—*e.g.*, insulating pitch, brewers' pitch, roofing pitch, etc.

2. *Abraham*,[21] 1918. . . .

3. *Mrazek*,[22] 1922.—Solid pitches, or Hoefer's asphaltites, are all black and very similar in appearance to coal, friable, of conchoidal break and brilliancy; these are in a great variety—raphaelite, grahamite, gilsonite, albertite, etc.

4. *Le Gavrian and Feret*,[25] 1923.—Residue from distillation of tar.

PYROBITUMENS.

1. *Richardson*,[14] 1908 (Summarised).—Native substances are relatively insoluble in the usual solvents for bitumen, and do not melt at comparatively low temperatures. On destructive distillation they give products similar to natural bitumens. They usually contain oxygen.

2. *Abraham*,[17] 1913.—Pyrobitumens: (*a*) Derived from the metamorphosis of vegetable growth—*e.g.*, peat, lignite, bituminous coal and anthracite coal; (*b*) derived from the metamorphosis of asphalts—*e.g.*, elaterite or wurtzilite, albertite and impsonite. [Examples of properties given.]

3. *Abraham*,[21] 1918.—A generic term, applied to native substances, of dark colour; comparatively hard and non-volatile; composed of hydrocarbons, which may

or may not contain oxygenated bodies; sometimes associated with mineral matter, the non-mineral constituents of which being *fusible* and relatively insoluble in carbon disulphide.

NOTE.—This definition includes the asphaltic and the non-asphaltic pyrobitumens, and their respective shales.

TAR.

1. *Abraham,*[17] 1913.—A dark coloured, bituminous substance, liquid or semi-liquid at room temperature, often possessing a characteristic "tarry" odour, usually insoluble in water, but miscible with carbon disulphide, benzole, etc., and which on distillation, oxidation, etc., forms a pitch. Its composition and origin are variable.

(*a*) Natural—*e.g.*, mineral tars or maltha.

(*b*) Artificial—the soft residues obtained: (1) From the distillation of petroleum—*e.g.*, petroleum tar or soft petroleum asphalt.

(2) From the destructive distillation of organic substances and pyro-bitumens—*e.g.*, pine tar, wood tar, bone tar, coal tar, mineral tar (maltha), petroleum tar, etc.

2. *Abraham,*[21] 1918. . . .

3. *Le Gavrian and Feret,*[25] 1913.—A substance produced by *destructive* distillation.

WAX.

1. *Abraham,*[21] 1918.—Mineral Wax. A term applied to a species of bitumen, also to certain pyrogenous substances; of variable colour viscous to solid consistency; having a *characteristic lustre* and *unctuous feel;* com-

paratively non-volatile; composed of hydrocarbons, substantially free from oxygenated bodies; containing *considerable crystallizable* paraffines; sometimes associated with mineral matter, the non-mineral constituents being easily fusible and soluble in carbon disulphide.

NOTE.—" . . . It is practically impossible to distinguish between certain native and pyrogenous asphalts or mineral waxes, either by physical or chemical means. . . . We must be content, therefore, to apply the terms 'asphalt' and 'mineral wax' both to native substances and to manufactured (pyrogenous) products."

2. *Abraham*,[21] 1918.—A term applied to unctuous, fusible and more or less viscous to solid substances, having a characteristic "waxy" lustre, and which are insoluble in water, but more or less soluble in carbon disulphide, benzole, etc. They are extremely susceptible to changes in temperature. Their composition, origin and colour are variable.

(*a*) Natural: (1) Mineral (*e.g.*, ozokerite, ceresine, montan wax, hatchellite, etc.).

(2) Vegetable (*e.g.*, Japan wax, carnauba wax, etc.).

(3) Animal (*e.g.*, beeswax, spermaceti, etc.).

(*b*) Artificial: (1) From the distillation of paraffinaceous petroleum, ozokerite, etc.

(2) From the destructive distillation of lignite (brown coal), paraffinaceous shales, etc.

INTER-RELATIONS.

The relationship of the main groups of substances to one another is shown in the following tables and "trees." With the remarks already made and the comments that follow there is no need for further introduction.

Richardson,[14] 1908 (Summarised):

BITUMENS:

Gas.

Petroleum.

Maltha : Transition products between oil and asphalt.

Solid Bitumens : Consisting largely of paraffine hydrocarbons, ozokerite, etc.

Consisting of unsaturated cyclic hydrocarbons, terpenes, fossil resin, amber, etc.

Derived from or originating in polymethylene petroleums, the more volatile components consisting of di- or tri-cyclic saturated hydrocarbons.

Asphalts : Trinidad, Venezuela, California, Cuba; Glance pitch.

Consisting largely of cyclic hydrocarbons attacked by strong sulphuric acid, but which otherwise are stable.

Manjak.

Gilsonite.

Grahamite : Rapidly shades into pyrobitumens.

PYROBITUMENS: Practically insoluble in chloroform or heavy petroleum.

Derived from petroleum hydrocarbons.

Albertite.

Wurtzilite.

Derived from direct metamorphosis of vegetable growth.

Anthracite.

Bituminous Coal.

Lignite.

Peat (?).

Holde,[16] 1912 (Summarised):

TECHNICAL BITUMENS.

A. NATURALLY OCCURRING.

- *I. Saponifiable.*
  - Mainly wax esters: (*a*) sapropel wax; (*b*) alga wax. Lignite bitumen (crude Montan wax). The waxes (*a*) and (*b*) are geologically the predecessors of the crude materials in A. II.
- *II. Unsaponifiable.*
  - Mainly hydrocarbons, fluid and solid bitumens, with oxidised and sulphurised hydrocarbons.
    - Natural gas.
    - Petroleum (fluid to viscous.)
      - Distillate.
      - Residue.
    - Wax: Ozokerite (solid) yielding ceresine, paraffin and oil.
  - Solid or viscous sulphurised or oxydised hydrocarbons, natural asphalt and tar. The first contains 0·8 to 12 per cent. sulphur, 1·5 to 35 per cent. oils, containing usually less than 1 per cent. paraffin.

B. Artificial Tars (by Destructive Distillation).

I. Lignite. II. Shale. III. Coal. IV. Wood. V. Fat. VI. Peat. VII. Oil Gas. VIII. Water Gas. IX. Bone, etc.

Abraham,[17] 1913:

BITUMINOUS SUBSTANCES.

- Natural
  - Bitumens
    - Gaseous
      - Natural Gas.
      - Marsh Gas.
    - Liquid
      - Petroleums
        - Paraffin Base.
        - Asphaltic Base.
        - Mixed Base.
      - Malthas (Mineral Tar)
        - Mixed Base.
    - Solid
      - Mineral Waxes
        - Ozokerite (Ceresine).
        - Montan Wax.
        - Hatchellite.
      - Mineral Pitches
        - Asphalt(um)
          - Pure or fairly pure.
          - Calcareous.
          - Siliceous.
          - Earthy.
        - Asphaltites
          - Gilsonite.
          - Glance Pitch.
          - Manjak.
          - Grahamite.
  - Pyrobitumens
    - Solid
      - Occur fairly pure
        - From Asphalts
          - Wurtzilite (Elaterite).
          - Albertite.
          - Impsonite.
        - From Vegetable Growths
          - Peat.
          - Lignite.
          - Bituminous Coal.
          - Anthracite.
      - Mineral matter pre-
        - Bituminous Schists.
        - Bituminous Shales.

BITUMINOUS SUBSTANCES.

(Continued.)

- Artificial
  - Animal Origin
    - From Bones
      - Bone Tar and Bone-Tar Pitch
    - From Fats
      - Fatty Acid Pitches “Stearine Pitch”
        - Stearine Pitch (“Candle Tar”).
        - Stearine-wool Pitch.
        - Wool-fat Pitch (“Wool Pitch”)
  - Vegetable Origin
    - From Vegetable Oils
      - —
        - Palm Oil Pitch.
        - Cotton-seed Oil Pitch.
        - Cotton-oil-foots Pitch.
    - From Saps of Coniferæ
      - Resin Pitch.
    - From Wood and Roots of Coniferæ
      - Pine Tar and Pine Tar Pitch.
    - From Hard Woods e g., Oak, Birch, and Beech
      - Wood Tar and Wood Tar Pitch.
  - Mineral Origin
    - From Petroleum.
      - Water Gas Tar and Water Gas Tar Pitch.
      - Sludge Pitch.
      - Petroleum Asphalt (Petroleum Pitch).
      - Blown (oxidised) Petroleum Asphalt
    - From Malthas
      - Asphalt(um).
    - From Ozokerite, etc.
      - Paraffin, etc.
    - From Peat
      - Peat Tar and Peat Tar Pitch.
    - From Lignite
      - Lignite Tar (Brown Coal Tar) and Lignite Tar Pitch.
    - From Bituminous Coal
      - Coal Tar and Coal Tar Pitch.
      - Coke Oven Tar and Coke Oven Tar Pitch.
      - Blast Furnace Tar and Blast Furnace Tar Pitch.
      - Generator Gas Tar and Generator Gas Tar Pitch.
    - From Elaterite
      - Elaterite Pitch.
    - From Bituminous Shales
      - Shale Oil and Shale Oil Pitch.

RESINOUS SUBSTANCES[4] (SUMMARISED).

Natural	True Resins	Common Resins. Fossil Resins.		
	Oleo Resins			
	Gum Resins			
	Mineral Resins	Ozokerite, etc. Asphalt(um). Asphaltites.		
Artificial	Animal Origin	From Bones	Bone Tar Pitch.	
		From Fats	Fatty Acid Pitch	“Stearine Pitch.”
	Vegetable Origin	From Vegetable Oils	Fatty Acid Pitch Oxidised Oils.	
		From Saps of Coniferæ	Resin Pitch.	
		From Wood and Roots of Coniferæ	Certain varieties of Pine Tar. Pine Tar Pitch.	
		From Hard Woods	Wood Tar Pitch.	
	Mineral Origin	From Petroleum	Water Gas Tar Pitch. Sludge Pitch. Petroleum Asphalts. Blown Petroleum Asphalts.	
		From Maltha	Asphalt(um).	
		From Peat	Peat Tar Pitch.	
		From Lignite	Lignite Tar Pitch.	
		From Bituminous Coal	Coal Tar Pitch. Coke-oven Tar Pitch. Blast-furnace Tar Pitch. Generator Gas Tar Pitch.	
		From Elaterite	Elaterite Pitch.	
		From Bituminous Shales	Shale Oil Pitch.	

Engler,[27] 1913 (Slightly summarised):

Fat, wax, resin, etc.: animal and vegetable residue.

↓

Sapropel. Faulschlamm.

↓

I. *Anabitumen*	Contains free fatty acids, wax esters, and hydrocarbons, adipocere, sapropel fat, ozokerite (?).
IIa. *Polybitumen*	Benzole-insoluble bitumen in Scotch shale, etc., containing high molecular, highly polymerised hydrocarbons and oxygenated compounds.
IIb. *Katabitumen*	Benzole-soluble bitumen of the Scottish and other schists; maltha, partially depolymerised polybitumens, decomposing further on heating.
III. *Ecgonobitumen*	All crude petroleums, depolymerised and broken-down hydrocarbons containing remains of Stages I. and II., further decomposed by distillation or heat.
IV. *Oxybitumens*	Asphalt, glance pitch, grahamite, albertite, gilsonite (?).

Abraham,[21] 1918 (Summarised):

BITUMINOUS SUBSTANCES.

- Bitumens
  - Petroleums
    - Non-asphaltic.
    - Mixed-base.
    - Asphaltic.
  - Native Mineral Waxes
    - Ozokerite.
    - Montan Wax.
  - Native
    - Pure or fairly pure.
    - Associated with mineral matter.
    - < 10 per cent. on dry material containing a substantial proportion of sand, sandstone, limestone, clay, or shale.
  - Asphaltites
    - Gilsonite — Extremely pure
    - Glance Pitch — Pure to moderately pure
    - Grahamite — Pure to quite impure
    - Higher fusion point than asphalts derived from petroleum.
- Pyrobitumens
  - Asphaltic Pyrobitumens
    - Elaterite
    - Wurtzilite
    - Albertite
    - Impsonite
    - Asphaltic Pyrobituminous Shales
    - Generally pure, infusible and insoluble. Derived from petroleum.
  - Non-asphaltic Pyrobitumens
    - Peat Shales.
    - Lignite.
    - Bituminous Coal.
    - Anthracite Coal.
    - Lignite and Coal Shales.
- Pyrogenous Distillates. . . .
- Pyrogenous Residues. . . .

Abraham himself points out (1913) how certain definitions overlap. It will be seen that "asphaltum" may be a natural bitumen, or natural mineral resin, or an artificial bitumen, or an artificial resin of mineral origin. The various tar pitches are artificial bitumens and resins; "asphaltites" and "mineral waxes" are natural mineral pitches and also mineral resins.

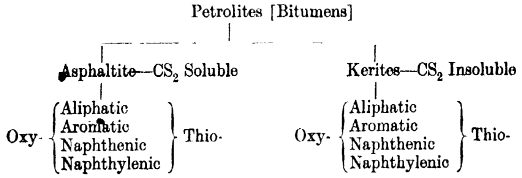
From his two schemes it is clear that the term "natural bitumen" covers everything from natural gas* to the heaviest portion petroleum, including bituminous rocks. "Natural pyrobitumens" covers albertite, etc., and the various coals; "artificial bitumen" (in the one, and "resinous substances" in the other) covers the various tars—a very wide range indeed.

Mrazek,[22] 1923:

(*a*) *Free* "bitumena":
1. Gaseous.
2. Liquid.
3. Solid: (*a*) paraffin; (*b*) ozokerite; (*c*) asphalt; (*d*) solid pitch (Hoefer's asphaltites).

(*b*) *Fixed* "bitumena": Bituminous schist, sapropelic coals.

Hackford,[24] 1922:



Le Gavrian and Feret,[25] 1923:

NATURAL PRODUCTS.		MANUFACTURED PRODUCTS.	
Bitumens	Maltha (viscous bitumens) Without qualification. Epurés. Paraffins.	Refined bitumen.	
		Residues (oils and residues)	Sulphurised. Oxidised (blown).
Asphalt	Without qualification. Consisting solely of asphaltic limestone. Sandstone. Shale.	Mastic.	
Ozokerites.		Ceresines.	
		Tar Products	Oils. Tars. Pitches.

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* This is specifically omitted from his classification of 1918.

It is not to be expected that these various authors have put forward their ideas without commenting on the schemes of others or drawing comments on their own.

Clifford Richardson,[26] in 1916, could see nothing reasonable in the British Committee's ideas, and considered them untenable from the American standpoint. They arose, he stated, from Great Britain's first acquaintance with asphalt roads having been made through rock asphalt. But it may be asked whether or not every country's first acquaintance was not so made.

Mrazek[22] pronounced Höfer's classification to be a great move forwards, but thought that subsequent more precise information justified another scheme—his own.

Le Gavrian and Feret,[25] 1923, considered Holde's scheme of 1912, and the A.S.T.M. definitions of 1918 to lack somewhat in clearness, and they welcomed the precision with which the British classification distinguished between "bitumen," "asphalt" and "tar," words which are so intermixed in the American scheme.

This exposition of the present state of the nomenclature shows the confusion and contradiction that exists, and it is to be hoped that in the near future orderliness and clear understanding will be attained, and this through restoration and pruning rather than through further extension and elaboration.